

Stereoselective Additions to Cyclopropenes

BY

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Submitted to the graduate degree program in Chemistry
and the Graduate Faculty of the University of Kansas in partial fulfillment of the
requirements for the degree of Doctor of Philosophy

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Stereoselective Additions to Cyclopropenes

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Date Approved: _____5/4/2018_____

Abstract

This thesis concerns strain-release driven stereoselective addition reactions to cyclopropenes leading to the synthesis of medium-sized 8-membered 1,5-dioxocane ring structures, optically active cyclopropylboronates, and densely functionalized cyclopropane scaffolds via the addition of highly reactive carbon nucleophiles. This thesis is separated into three chapters detailing the background, development, optimization, scope, and limitations of each developed methodology.

Chapter one describes a strain-release driven nucleophilic (4+4) cycloaddition of cyclopropenes providing a fused three ring system possessing a medium-sized eight member ring core. The process is believed to proceed via a face-selective nucleophilic attack of an alkoxide on the strained double bond of cyclopropene followed by highly diastereoselective nucleophilic ring closure. Additionally, a newly developed expedited and cost saving method of accessing prochiral cyclopropenes possessing an unsubstituted double bond via Rh(II)-catalyzed [2+1] cycloaddition is detailed.

Chapter two describes the directed rhodium(I)-catalyzed asymmetric hydroboration of cyclopropenes bearing ester and amide functions as directing groups. Hydroboration of esters provided variable results sensitive to the identity of the substituent on the opposing face of cyclopropene. The utilization of a much more Lewis basic amide function as a highly efficient directing group along with the development of a new class of prochiral cyclopropenyl amides is detailed.

Chapter three describes the directed copper(I)-catalyzed ring retentive addition of Grignard reagents across the strained double bond of cyclopropenes. The high degree of conformational and configurational stability of the intermediate cyclopropyl Grignard reagent allowed for highly diastereoselective trapping with a variety of electrophiles, providing the possibility of constructing two carbon-carbon bonds and up to four contiguous stereocenters in a single chemical step.

Acknowledgments

I would first like to express my gratitude for my advisor Michael Rubin. Your support, advice, insight, and critiques have played an integral role in my education and development as a chemist. The last five years have not been without struggle but have also consisted of many “good job” quotes and high-fives. I thank you for allowing me to conduct research as a part of your group and will always look back on this opportunity with many fond memories.

I thank my teachers at KU: Prof. Mike Clift, Prof. Tim Jackson, Prof. Michael Rubin, Prof. Helena Malinakova, and Prof. Paul Hanson. Your classes were always stimulating and thought provoking.

I would like to thank my oral proposal and thesis committee members: Prof. Jon Tunge, Prof. Paul Hanson, Prof. Misha Barybin, Prof. Blake Peterson, and Prof. Michael Rubin.

I owe a great deal of thanks to Dr. Pasha Ryabchuk. As the person who initially got me interested and excited about organic chemistry, introduced me to the lab, and taught me countless techniques including how to set up a reaction, run a column, characterize a compound, and even do a paper towel extraction, this thesis may not have been possible without your enthusiasm and guidance.

I thank everyone who I have worked with in the lab. I would like to specifically acknowledge Vlad Maslivets for understanding the struggle and Mike Lu-Diaz, Trevor Bennin, and Chandler Coleman for being excellent undergraduate researchers. I thank Hillary Straub for your selfless assistance while I recovered from injury. Your willingness to help means a lot to me.

Kaitie Cartwright deserves special recognition. You made this grueling process enjoyable and always offered support and encouragement in my moments of doubt. I am very grateful for everything you have done.

Thank You.

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List of Abbreviations

18-C-6	1,4,7,10,13,16-Hexaoxacyclooctadecane
9-BBN	9-Borabicyclo[3.3.1]nonane dimer
Ac	Acetyl
ACS	American Chemical Society
aq.	Aqueous
Ar	Aryl ring
B ₂ Pin ₂	Bis(pinacolato)diboron
<i>c</i> -heptyl	Cycloheptyl
CAHB	Catalytic asymmetric hydroboration
Cat.	Catalyst
CDI	1,1'-Carbonyldiimidazole
cm ⁻¹	Inverse centimeters
Cy	Cyclohexyl
d	doublet (NMR)
DBU	1,8-Diazabicyclo(5.4.0)undec-7-ene
DCC	N,N'-Dicyclohexylcarbodiimide
DCM	Dichloromethane
DG	Directing group
DIAD	Diisopropyl azodicarboxylate
DIBAL-H	Diisobutylaluminum hydride
DMA	Dimethylacetamide
DMAP	4-dimethylaminopyridine
DME	Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
dr	Diastereomeric ratio

List of Abbreviations (Continued)

EDC	N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide
equiv.	Equivalents
er	Enantiomeric ratio
Et	Ethyl
FTIR	Fourier transform infrared spectroscopy
g	Gram
GC	Gas chromatography
h	Hour
Hz	Hertz
L _n *	Asymmetric ligand
HBPIn	Pinacol borane
HBTU	2-(1 <i>H</i> -benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
HCTU	2-(6-Chloro-1- <i>H</i> -benzotriazole-1-yl)-1,1,3,3-tetramethylaminium hexafluorophosphate
HOBt	1-Hydroxybenzotriazole
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry
m	Multiplet (NMR)
Me	Methyl
MeCN	Acetonitrile
CD ₃ OD	Deuterated methanol
MeOH	Methanol
MHz	Megahertz
[MI]	Migratory insertion
min	Minute
MOMCl	Methoxymethyl chloride

List of Abbreviations (Continued)

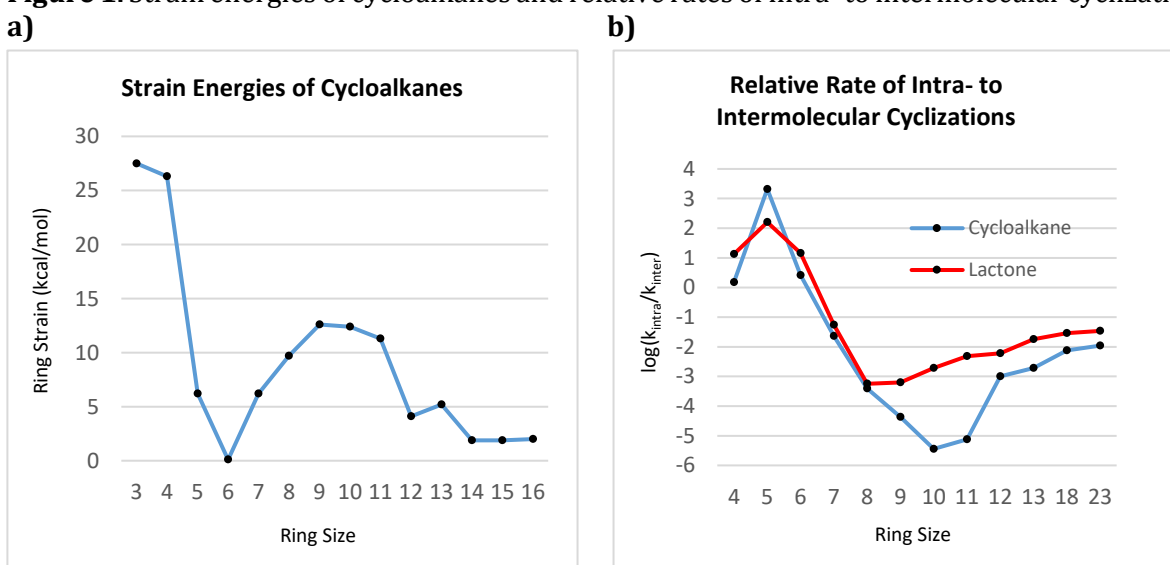
mp	Melting point
MTBE	Methyl tert-butyl ether
<i>n</i> -Bu	Butyl
NMR	Nuclear magnetic resonance
Nuc	Nucleophile
[OA]	Oxidative addition
ORTEP	Oak Ridge thermal ellipsoid plot
<i>p</i> -TsOH	<i>p</i> -toluenesulfonic acid
Ph	Phenyl
PhMe	Toluene
Pyr.	Pyridine
q	Quartet (NMR)
[RE]	Reductive elimination
R.O.P.	Ring opened product
R _f	Retention factor
R _t	Retention time
RT	Room temperature
s	Singlet (NMR)
t	Triplet (NMR)
TBDMSCl	<i>tert</i> -Butyldimethylsilyl chloride
tBuOK	Potassium <i>tert</i> -butoxide
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TM	Transition metal
TMS	Trimethylsilyl
Ts	Tosyl

Chapter 1. Strain-Release Driven (4+4) Cyclodimerization of Cyclopropenes

1.1 Introduction

Medium-sized rings are considered to be those between 7 and 11 members. These structures are widely found in various natural products,^[1] pharmaceuticals,^[1] and materials science.^[2] Despite their well-known biological and industrial applications, methods for direct cyclization are quite rare. Nucleophilic closure of medium-sized rings is considerably more challenging than assembly of five-, six-, and twelve-membered and even larger analogs. This is due to an increase in ring strain (enthalpic barrier) and a significant loss in conformational freedom (entropic barrier) accompanying such cyclizations. The inherent strain energy of cycloalkanes (**Figure 1a**)^[3] rapidly decreases from a maximum with cyclopropane to essentially none with cyclohexane, mostly due to a relaxation of bond angle distortion. However, the strain of rings then increases between seven and eleven members and can be attributed to the development of transannular strain. In many cases, the rate of intramolecular head-to-tail cyclization forming medium-sized rings becomes considerably slower than the undesired intermolecular polymerization reaction (**Figure 1b**).^[4]

Figure 1. Strain energies of cycloalkanes and relative rates of intra- to intermolecular cyclization.



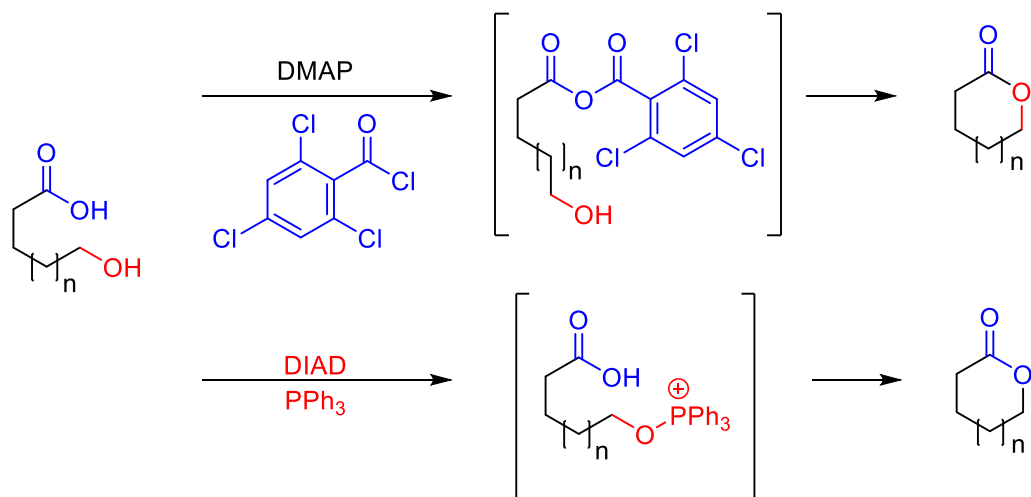
To achieve acceptable reaction efficiency, substrate activation is typically required to overcome the two inhibitory barriers (enthalpic and entropic) opposing medium-sized ring synthesis. Two of the oldest and most widely used methods were developed by Yamaguchi^[5] and Mitsunobu,^[6] in which either a carboxylic acid or alcohol terminus are activated by conversion to the corresponding intermediate mixed anhydride or oxyphosphonium ion respectively (**Scheme 1a**).

More recently, Rousseau^[7] has shown that a variety of electrophilic iodine reagents sufficiently activate olefins toward macroiodolactonizations (**Scheme 1b**). In a classic example by Corey and Nicolaou,^[8] double activation of a substrate was achieved by converting a carboxylic acid into a strategically designed thioester, which could then efficiently perform intramolecular deprotonation of the alcohol, simultaneously activating both termini toward cyclization (**Scheme 1c**).

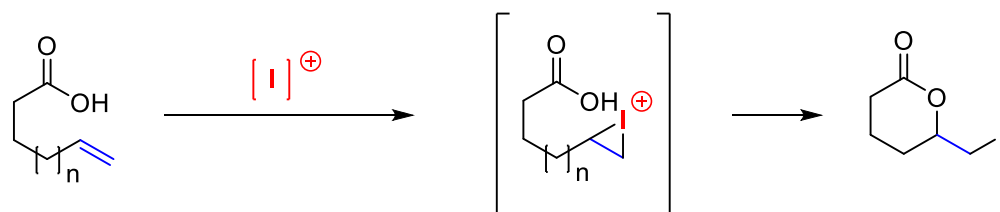
We envisioned our own mode of double activation toward the synthesis of medium-sized rings utilizing cyclopropenemethanol derivatives. Simple deprotonation would activate the alcohol while the inherent ring strain of cyclopropene would facilitate efficient nucleophilic ring closure (**Scheme 2**).

Scheme 1.

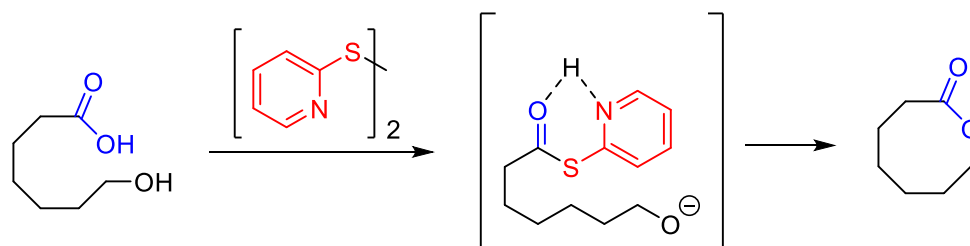
a)



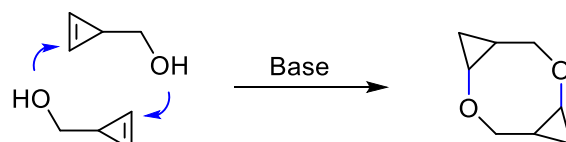
b)



c)



Scheme 2.

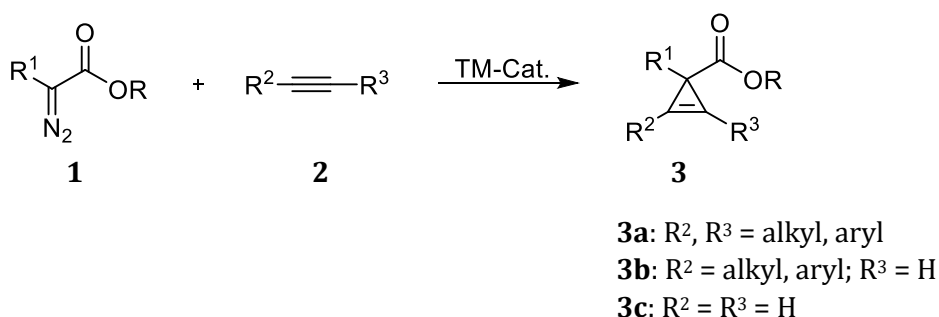


1.2 Synthesis of Cyclopropenes

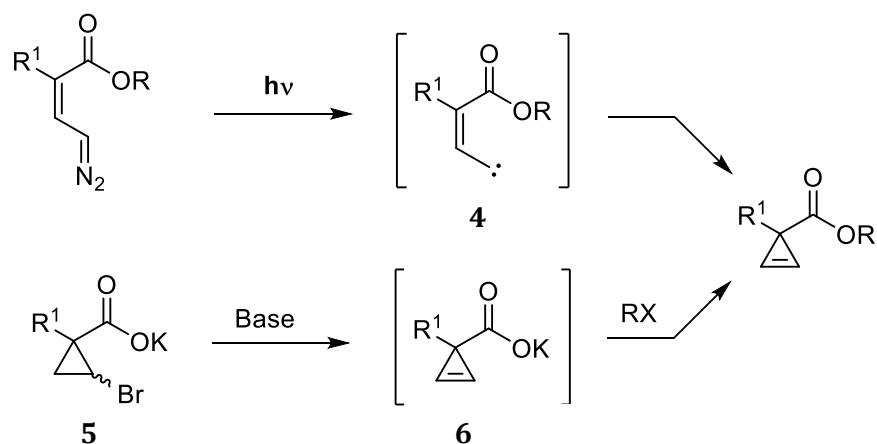
1.2.1 Introduction

To begin thorough evaluation of nucleophilic (4+4) cyclodimerization of cyclopropenes, it was quickly found that development of a protocol providing expedited access to 1-arylcycloprop-2-ene carboxylates possessing an unsubstituted double bond was necessary. Such structures are typically accessed via metal-catalyzed cycloadditions of carbenoids generated from diazoesters **1**, to various acetylenes **2** to provide ‘internal’ and ‘terminal’ cyclopropenes (**3a** and **3b** respectively), which have applications as strained chiral building blocks (**Scheme 3**).^[9]

Scheme 3.



Scheme 4.



However, prochiral cyclopropenes **3c** with an unsubstituted double bond, are often underutilized due to limited availability. Classical routes toward 3,3-disubstituted cyclopropenes include a photoinduced isomerization of vinylcarbenes **4**^[10] and 1,2-dehydrohalogenation of 2-bromocyclopropylcarboxylate salts **5**,^[11] followed by esterification of intermediate cyclopropene carboxylate **6** (**Scheme 4**).

Direct Rh(II)-catalyzed cyclopropenation of acetylene gas has also been reported,^[12] but has seen only limited application due to the inherent difficulties of handling gaseous reagents. Gevorgyan^[13] first reported the preparation of 1-phenylcycloprop-2-enecarboxylate via cyclopropenation of trimethylsilylacetylene with phenyldiazoacetate followed by removal of TMS. However, to access the necessary starting materials to evaluate the (4+4) nucleophilic cyclodimerization of cyclopropenes, a more general, scalable, and efficient protocol was required.

1.2.2 Results and Discussion

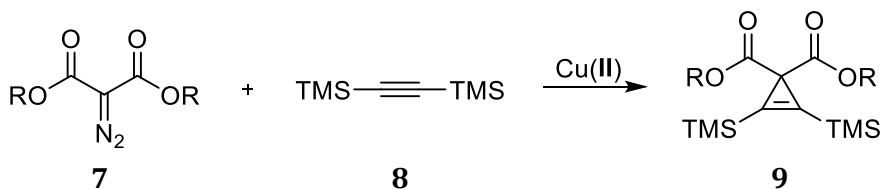
The use of bis(trimethylsilyl)acetylene **8** and trimethylsilylacetylene **11** as a substitute for acetylene gas in copper-catalyzed cyclopropenations^[14] of diazomalonates **7** has been known for some time (**Scheme 5a**). To access the desired 3,3-disubstituted cyclopropenes (**Scheme 3**, R¹ ≠ CO₂R), a Rh(II)-catalyzed transformation was chosen due to their precedent^[15] as catalysts for cyclopropenation of phenyldiazoacetates **10** and trimethylsilylacetylene **11** (**Scheme 5b**). However, this reaction proved to be very sluggish and only provided acceptable yields when a dilute solution of phenyldiazoacetate dissolved in TMS-acetylene was added to solvent quantities of neat TMS-acetylene and Rh(II)-catalyst by slow (<0.25 mL/h) syringe pump addition.

It was found that the large excess of TMS-acetylene could almost completely be recovered by direct distillation from the reaction mixture following reaction completion. The high volatility of TMS-acetylene, when compared to bis(trimethylsilyl)acetylene, allowed for efficient recovery

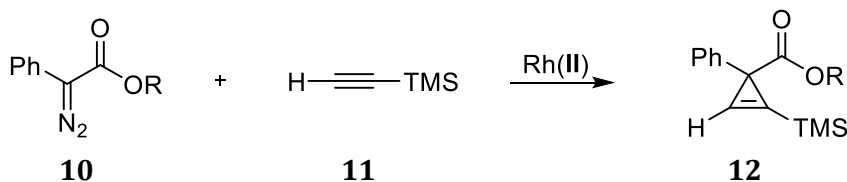
and reuse in subsequent reactions which was critical to the scalability of this protocol because using solvent level quantities of expensive TMS-acetylene was deemed cost prohibitive.

Scheme 5

a)



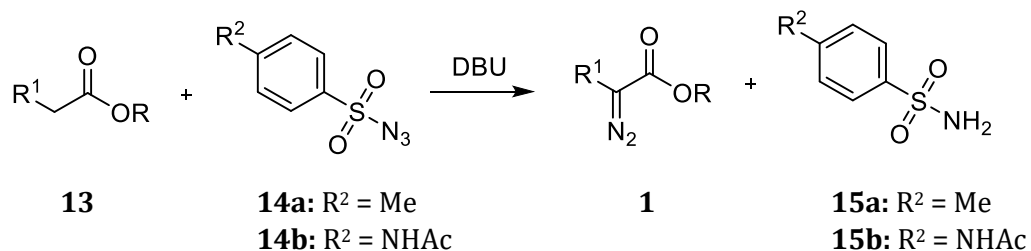
b)



The most straightforward synthesis of diazoesters **1** utilizes sulfonylazides **14a** to transfer a diazo function to activated methylene species **13** under basic conditions (**Scheme 6**). A result of this process is the generation of stoichiometric quantities of sulfonamide **15a** which, due to solubility and polarity issues, cause considerable complications with efficient purification.

Davies^[16] has reported the use of 4-acetamidobenzenesulfonylazide **14b** as an easily separable, although considerably more expensive, diazo transfer reagent. Due to the quantities of starting material envisioned to complete our investigation of (4+4) cyclodimerization of cyclopropenes, we sought a robust preparative protocol providing **12** utilizing the inexpensive and readily accessible p-tolyl substituted diazo transfer reagent **14a**.

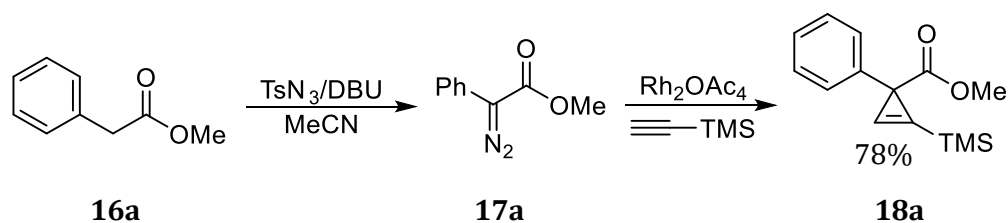
Scheme 6.



The synthesis of cyclopropenes **12** by Rh(II)-catalyzed cycloaddition, requiring the use of TMS-acetylene both as a reagent and a solvent, strictly limits the array of diazoesters able to undergo this transformation to those which are stable, non-polar, and display a high degree of solubility in TMS-acetylene. Initial studies were conducted using methylphenylacetate **16a** and tosylazide **14a** in the presence of DBU (**Scheme 7**). After sufficient optimization, it was found that careful washing of the product with saturated aqueous ammonium chloride and quick vacuum filtration through silica gel using hexanes could provide roughly purified diazoester **17a**, which showed approximately 80% assay by NMR analysis. This extremely expedited purification protocol, while completely removing the tosylamine byproduct, still gave a diazoester product possessing considerable insoluble impurities.

Interestingly, it was found that these impurities could easily be removed by dissolving the crude product in TMS-acetylene and withdrawing the supernatant solution into a syringe through a cotton wrapped needle. This syringe could then directly be used to deliver diazoester **17a** by syringe pump addition to refluxing solution of Rh(II) acetate in TMS-acetylene. These extremely expedited purification conditions provided cyclopropene **18a** in equivalent yield (78% vs 80%) to established procedures using diazoesters in fully and laboriously purified form (Scheme 7).^[17]

Scheme 7.



The developed protocol (Method A) which provided an expedited and efficient path to previously difficult to obtain substrates **18**, was then applied to a variety of diazoarylacetaes **16** which proved to be sufficiently soluble in TMS-acetylene (**Table 1**). It was found that chlorinated and brominated diazoarylacetaes exhibited decreased solubility and thus required higher dilution in TMS-acetylene for efficient syringe pump addition. Furthermore, fluorinated substrates were generally more soluble and in most cases good yields were obtained (**Table 1**).

For diazo compounds which were found to be poorly soluble in TMS-acetylene, an alternative method (Method B) was developed which relies on very slow continuous extraction to deliver diazoacetates to the reaction. In method B, the crude solid diazoesters **17f** and **17g** were placed into a piece of filter paper which had been rolled into cone and then set within a typical addition funnel. The addition funnel was then topped with a water cooled reflux condenser and then placed on top of a round bottom flask containing $\text{Rh}_2(\text{OAc})_4$ in refluxing TMS-acetylene (**Figure 2**).

Table 1. Synthesis of TMS-protected cyclopropenes via method A.

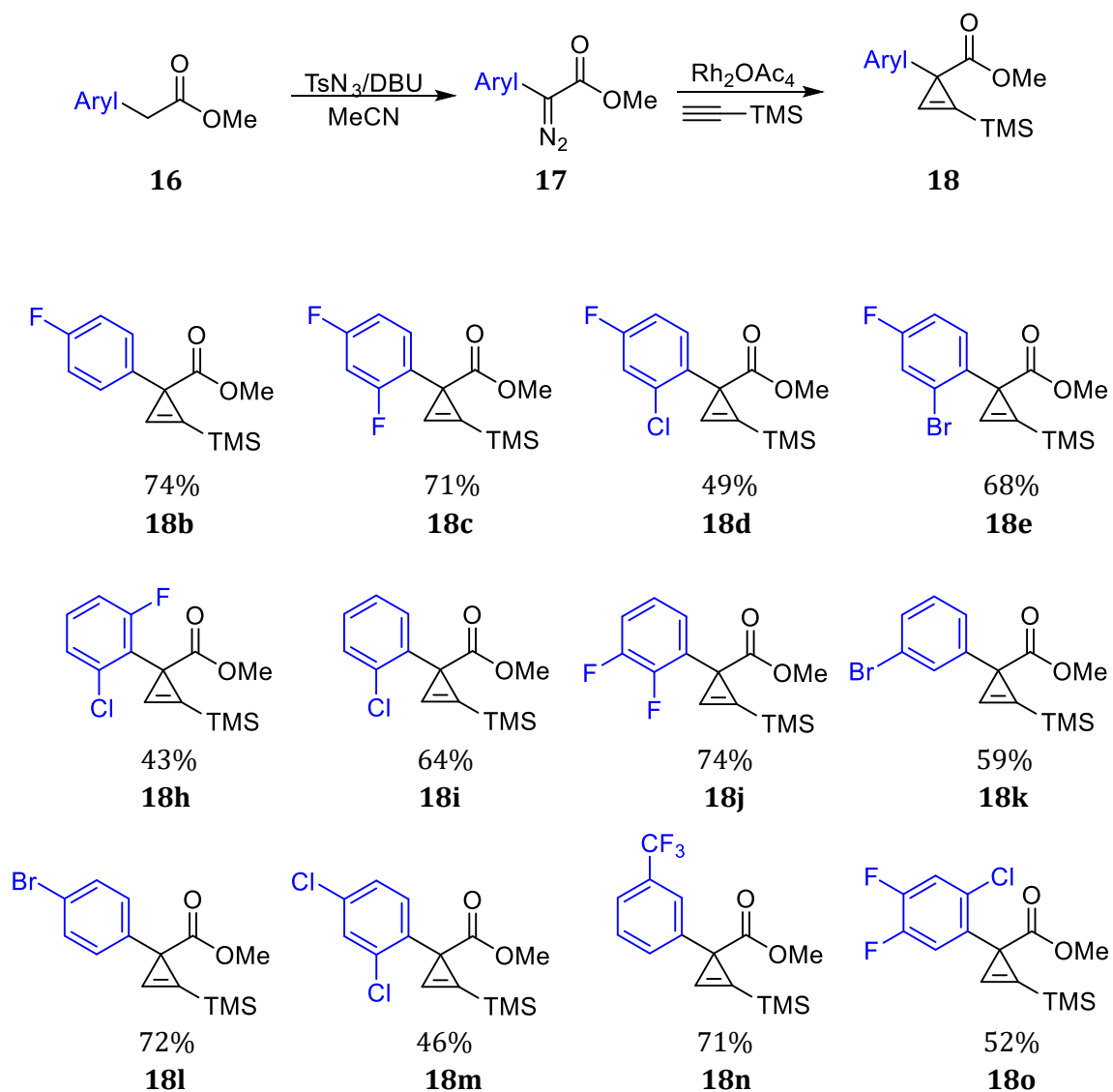
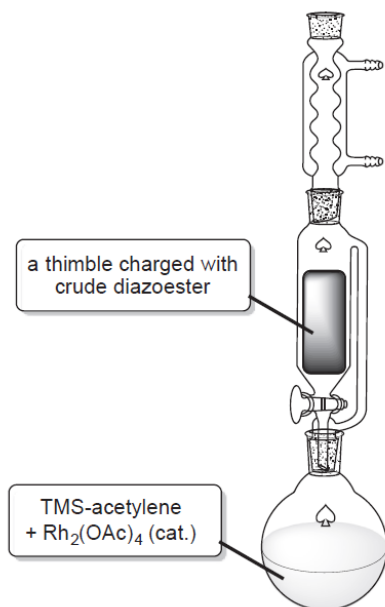
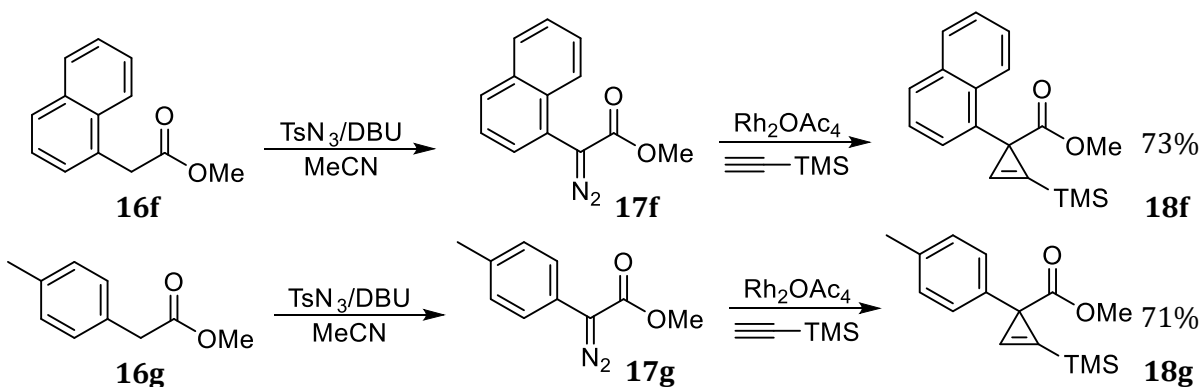


Figure 2. Schematic of continuous extraction apparatus.



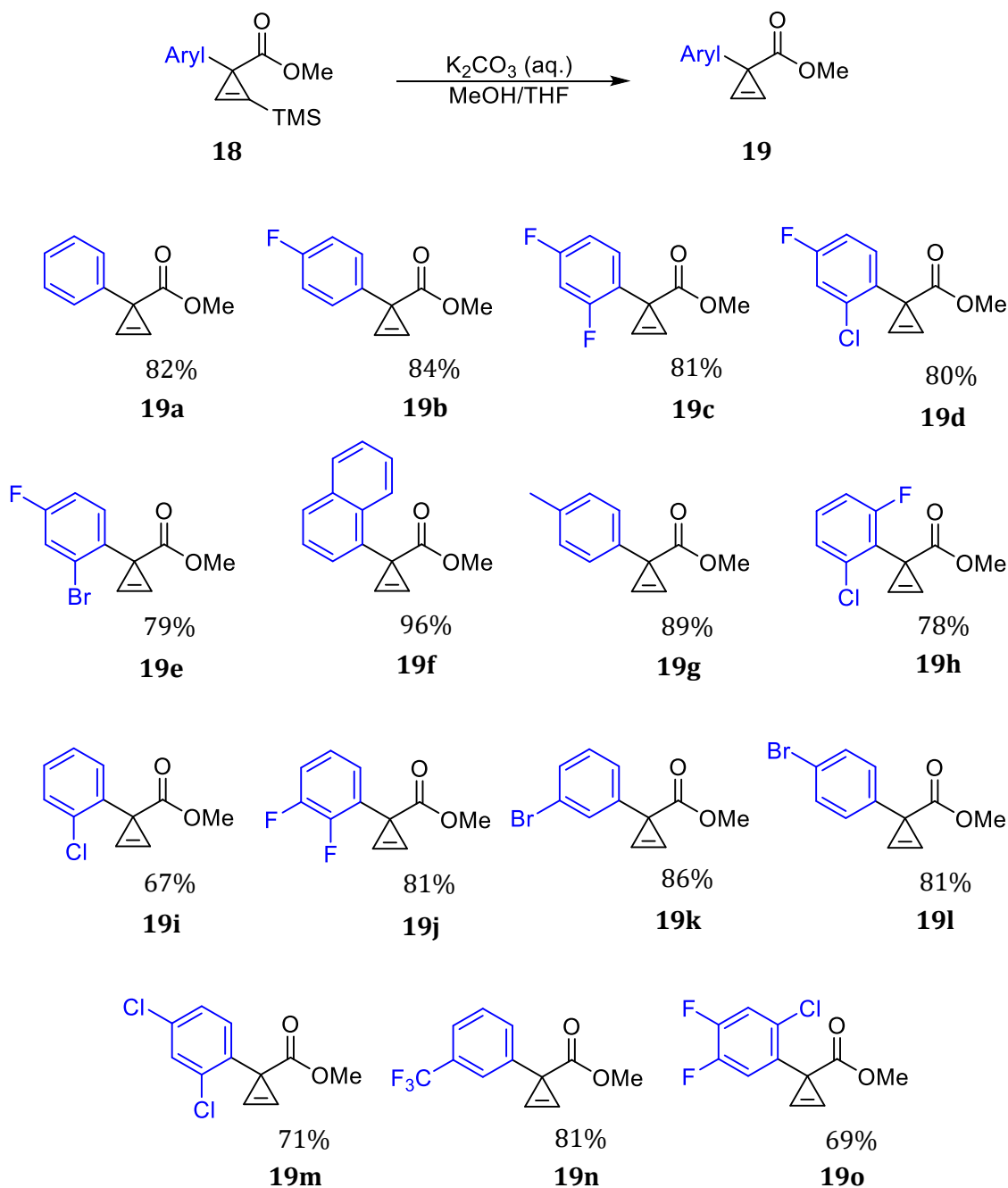
In this setup, a dilute solution of diazoester is slowly washed into the lower flask by condensing vapors of TMS-acetylene. This process allows for slow and steady dropwise delivery of diazoester into the reaction flask and offered far superior efficiency when compared to a typical Soxhlet apparatus, in which periodic syphoning of large volumes of relatively concentrated diazoester are added. This newly developed protocol was employed to synthesize cyclopropenes **18f** and **18g** in good yield (**Scheme 8**).

Scheme 8.



All TMS-protected cyclopropenes **18** could efficiently be desilylated by aqueous potassium carbonate while preserving the strained double bond and ester function to provide prochiral cyclopropenes **19** (Table 2).

Table 2. Desilylation of protected cyclopropenes.



1.3 Optimization of (4+4) Cyclodimerization of Deprotected Cyclopropenes

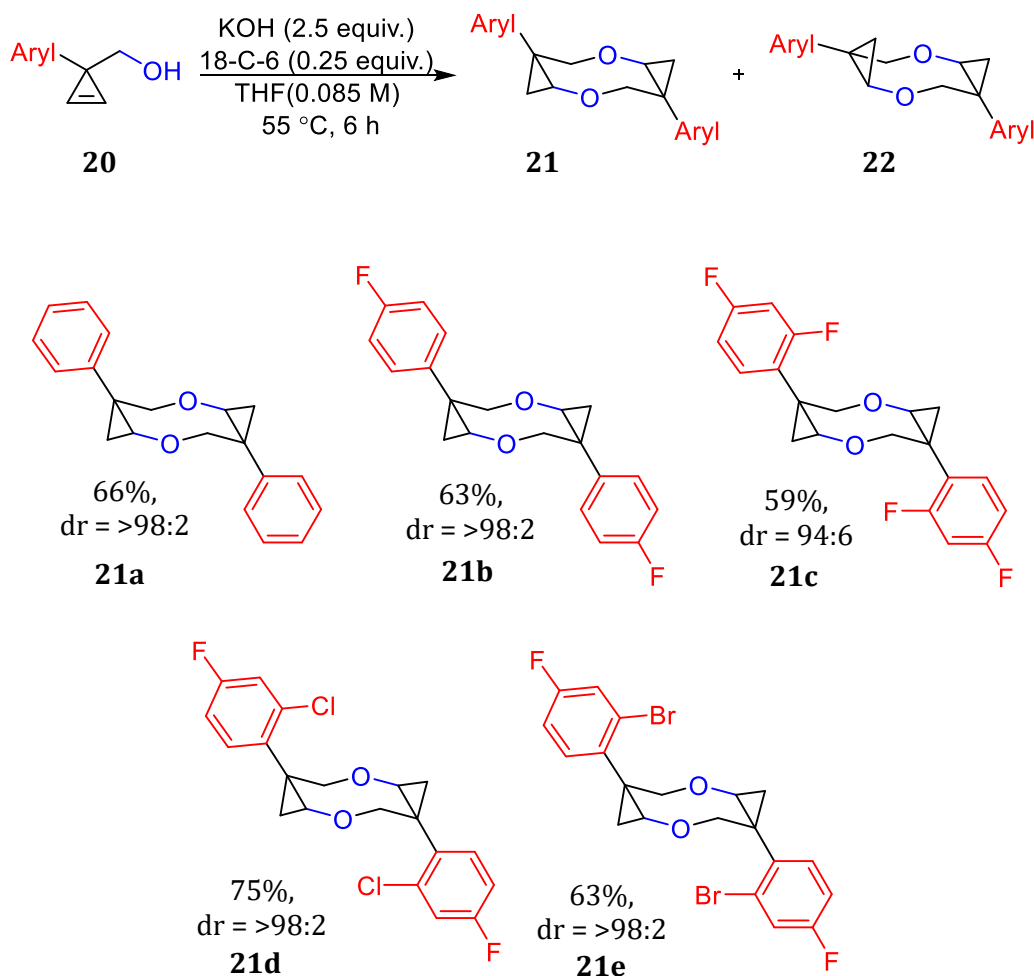
Initial attempts to achieve the desired (4+4) cyclodimerization reaction involved exposure of cyclopropene **20a** to conditions previously developed for addition of various alkoxide nucleophiles to cyclopropenes.^[18] Exposure of **20a** to *t*-BuOK in THF at 55 °C for six hours resulted in the selective formation of the eight membered homodimerization product **21a** in 70% yield as a single diastereomer (**Table 3, entry 1**)! Interestingly, no detectable evidence of the tert-butoxide addition product was observable by crude NMR analysis.

Replacement of *t*-BuOK with freshly powdered KOH under the same reaction conditions improved the reaction yield to as high as 74% while maintaining the exclusive diastereoselectivity (**Table 3, entry 2**). Concentrating the reaction drastically shortened reaction times and reactions performed in THF resulted in no observable cyclodimerization product most likely due to an increased propensity toward intermolecular polymerization (**entries 5-8**). Further dilution of the reaction had little effect on the transformation and only resulted in a substantial increase in reaction time (**entries 9, 10**). It was also found that polar aprotic well coordinating solvents resulted in substantial deterioration in diastereoselectivity (**entries 3, 4, 7, 8, 11-14**). Diethyl ether and toluene provided high selectivity but rather disappointing yields (**entries 15-18**). Reactions performed in dichloromethane, carbon tetrachloride, and 1,4-dioxane did not provide any observable product (**Table 3, entries 19 - 24**).

1.4 (4+4) Cyclodimerization of Deprotected Cyclopropenes

With optimized conditions established, the preparative scale reaction was evaluated across several substrates. In addition to **21a**, the 4-fluoro- **21b**, 2,4-difluoro- **21c**, 2-chloro-4-fluoro- **21d**, and 2-bromo-4-fluoro- **21e** analogs were obtained in good yields (**Table 4**).

Table 4. (4+4) cyclodimerization of deprotected cyclopropenes.

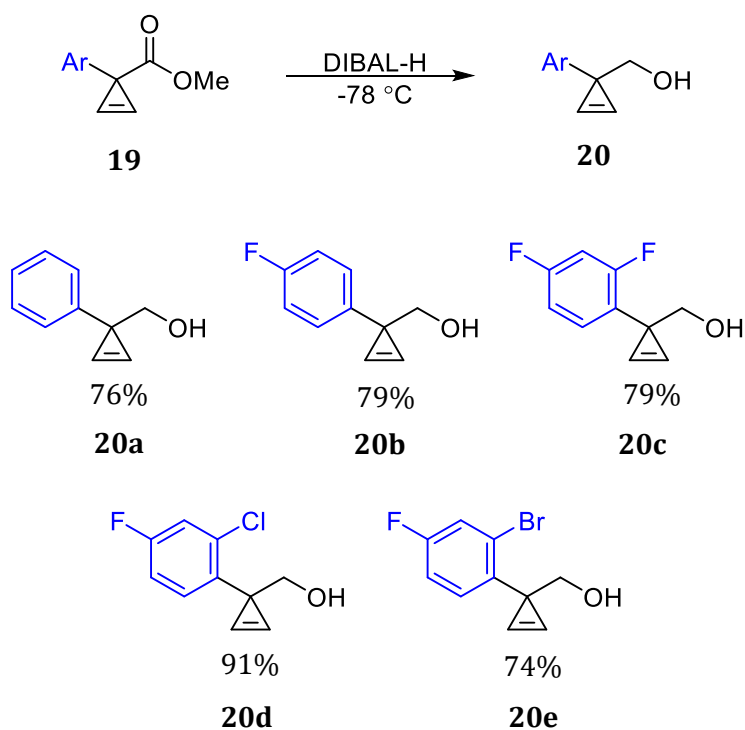


1.5 Optimization of Starting Material Synthesis

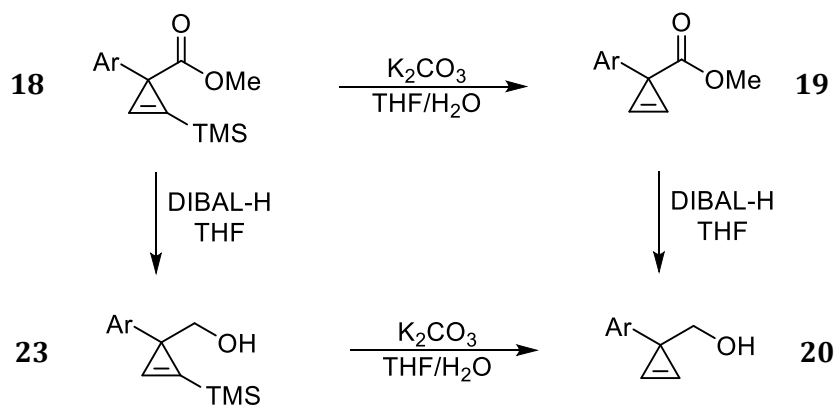
During the synthesis of starting materials to fully evaluate the scope of nucleophilic (4+4) cyclodimerization, it was found that cyclopropenes **18** could be efficiently desilylated with

potassium carbonate in a biphasic mixture of water and THF (**Scheme 2**). However, subsequent attempts to selectively reduce the ester function in the presence of the unprotected strained double bond proved quite challenging. Significant optimization involving the extremely slow addition of DIBAL-H to cyclopropenes **19** at -78 °C eventually provided acceptable yields of cyclopropenemethanols **20a-e** (**Table 5**). In an attempt to obtain structures **20a-e** in a more efficient and milder sequence, it was found that the order of desilylation/reduction could be swapped (**Scheme 9**).

Table 5. Reduction of deprotected cyclopropenylcarboxylates.

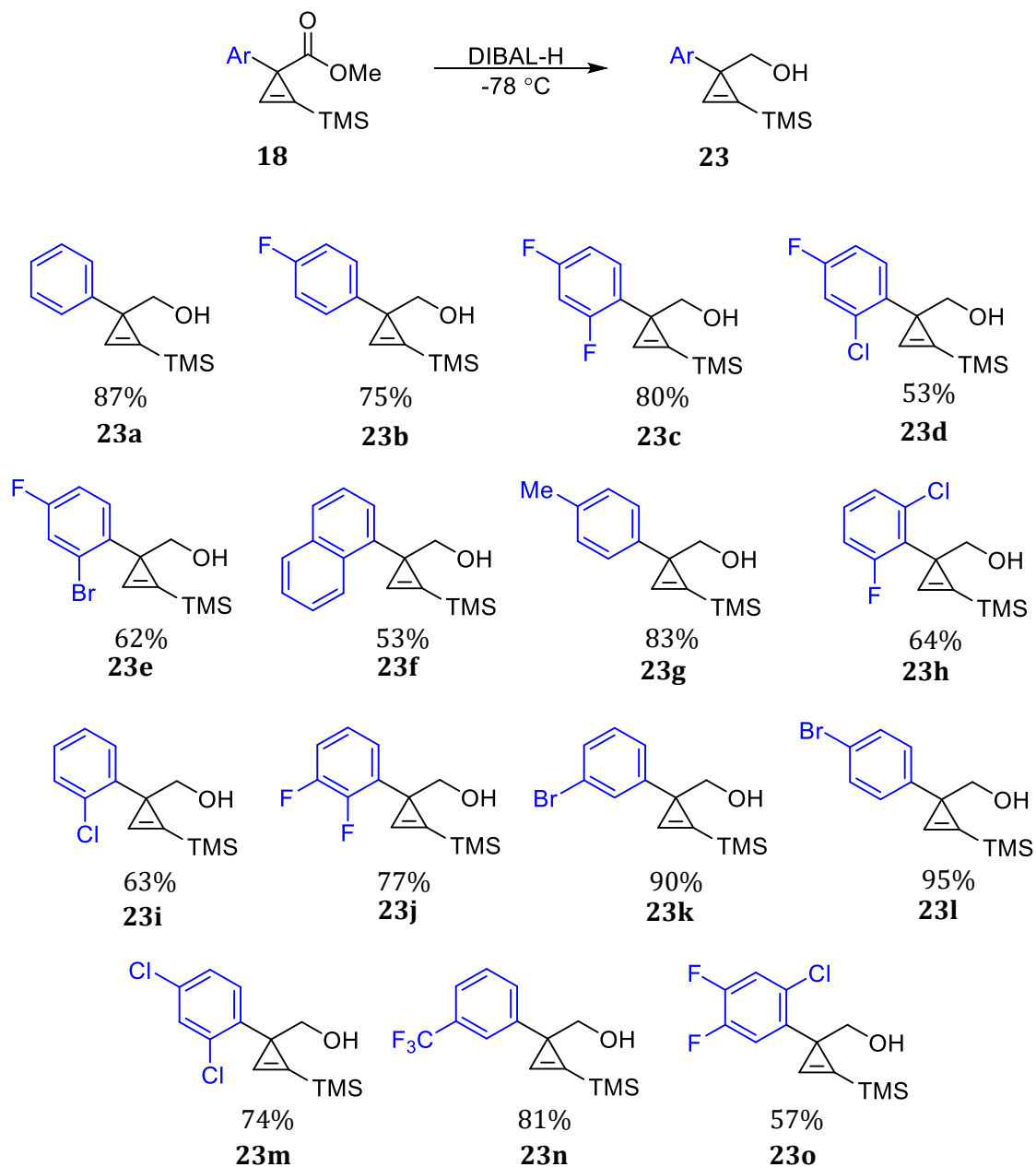


Scheme 9



While it was found that reaction conditions were required to be held at -78 °C to achieve conversion of **18** to **23**, the presence of the TMS protecting group during reduction provided improved yields in most cases (**Table 6**). However, this slight increase in efficiency was squandered by the subsequent deprotection step which typically did not provide yields above 50%, most likely due to prolonged exposure of a hydroxyl group to the strained electrophilic double bond of cyclopropene under basic conditions.^[18]

Table 6. Reduction of TMS-protected cyclopropenylcarboxylates.

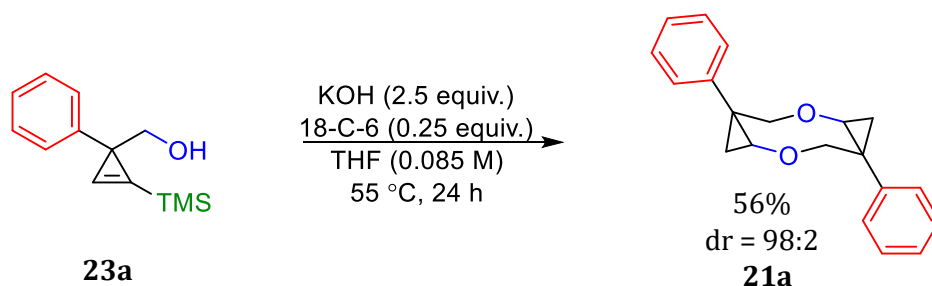


1.6 Optimization of One-Pot Desilylative (4+4) Cyclodimerization

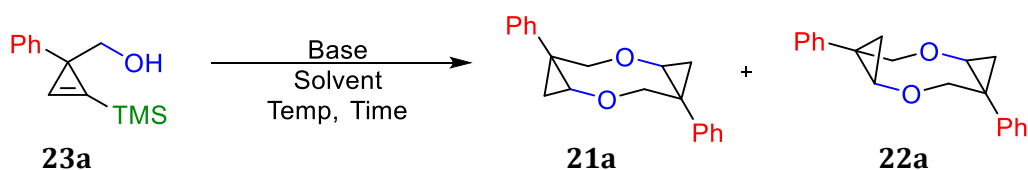
To overcome the synthetic bottleneck observed while attempting to access structures **20**, a one-pot desilylative/nucleophilic addition process providing 1,5-dioxocane **21a** directly from

cyclopropene **23a** was evaluated under the previously optimized reaction conditions for cyclization of cyclopropenes **20** (Scheme 10). Interestingly, the reaction did proceed to provide **21a** in somewhat reduced yield but still with a high degree of diastereoselectivity.

Scheme 10



Subsequent optimization of the new direct route toward 1,5-dioxocanes **21** found that any lowering of reaction temperature below 55 °C resulted in sharp declines in chemical yield (Table 7, entries 1, 2). Furthermore, increasing temperature to 65 °C offered a substantial gain in efficiency while further increasing the temperature to just 75 °C once again sharply decreased yield and even began to erode diastereoselectivity (entries 4, 5). Due to the process now requiring base, not only deprotonate the alcohol but also remove the TMS protecting group, increasing the base loading to five equivalents further increased yield to 77% (entries 6-8). As was observed in optimization with **20a**, reactions conducted with KOH and t-BuOK in a variety of other solvents offered reduced efficiencies and selectivities (entries 10-21). In all cases, the one-pot transformation proved to be somewhat slower, requiring reaction times of 24 hours and as long as 72 hours for reactions conducted in DMF and toluene (Table 7, entries 12-15, 20, 21).

Table 7. Optimization of one-pot desilylative (4+4) cyclodimerization.

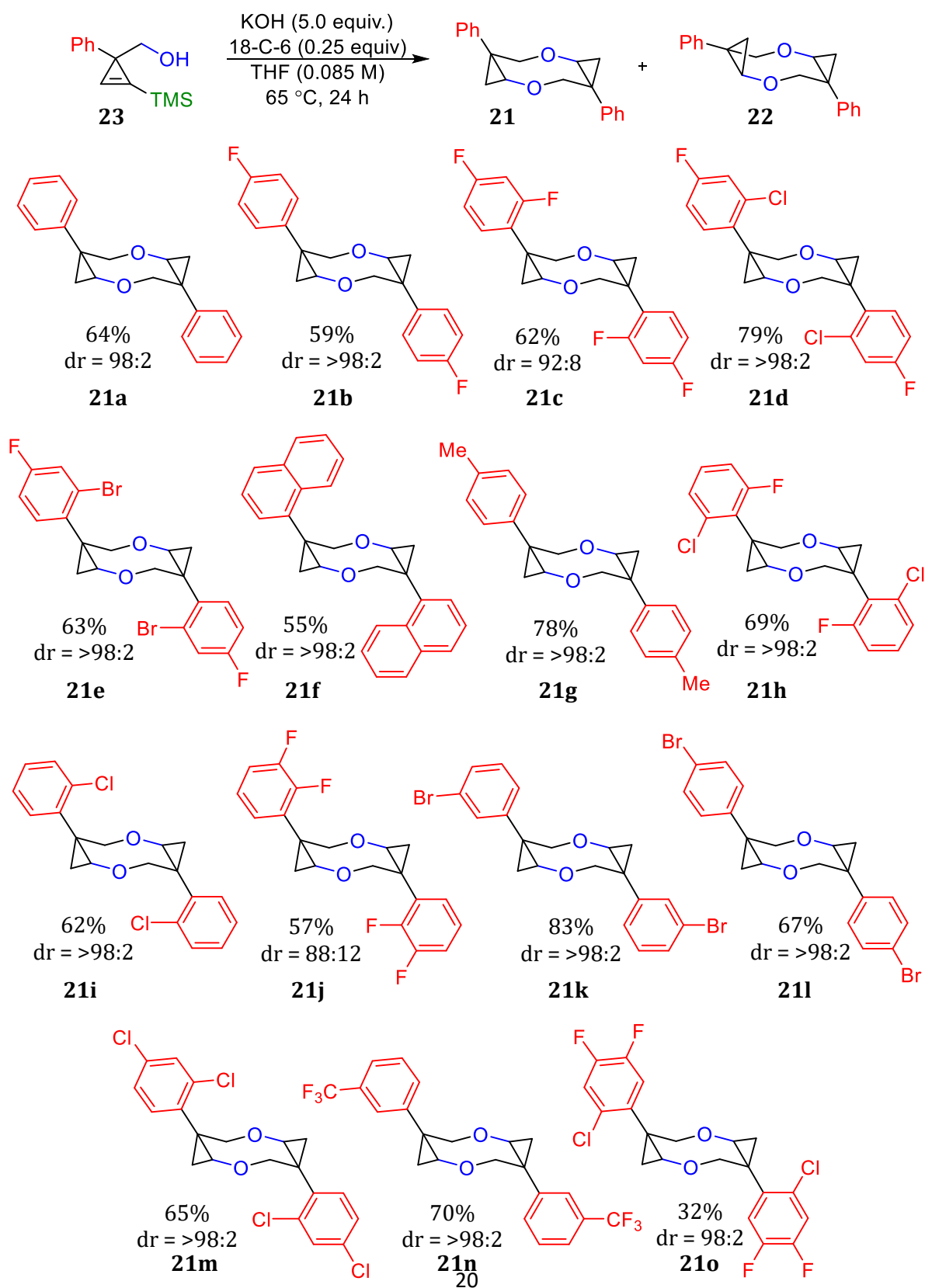
#	Base (equiv.)	Solvent (0.085 M)	Temp (°C)	Time (h)	Yield ^[a] , %	dr
1	KOH (2.5)	THF	35	24	0	-
2	KOH (2.5)	THF	45	24	21	98:2
3	KOH (2.5)	THF	55	24	56	98:2
4	KOH (2.5)	THF	65	24	68	98:2
5	KOH (2.5)	THF	75	24	49	97:3
6	KOH (1.5)	THF	65	24	45	98:2
7	KOH (5.0)	THF	65	24	77	98:2
8	KOH (7.5)	THF	65	24	75	98:2
9	<i>t</i> -BuOK (5.0)	THF	65	24	70	99:1
10	KOH (5.0)	DMSO	65	24	45	86:14
11	<i>t</i> -BuOK (5.0)	DMSO	65	24	67	87:13
12	KOH (5.0)	DMF	65	24	29 ^[b]	94:6
13	<i>t</i> -BuOK (5.0)	DMF	65	24	29 ^[b]	91:9
14	KOH (5.0)	DMF	65	72	34 ^[b]	93:7
15	<i>t</i> -BuOK (5.0)	DMF	65	72	21 ^[b]	92:8
16	KOH (5.0)	DMA	65	72	54	93:7
17	<i>t</i> -BuOK (5.0)	DMA	65	72	48	92:8
18	KOH (5.0)	Et ₂ O	65	24	59	99:1
19	<i>t</i> -BuOK (5.0)	Et ₂ O	65	24	61	99:1
20	KOH (5.0)	PhMe	65	72	71	98:2
21	<i>t</i> -BuOK (5.0)	PhMe	65	72	75	98:2

[a] NMR yields using dibromomethane as standard [b] Incomplete conversion: GC analysis showed presence of unreacted starting material **23a**. Test reactions were performed in 9.3 mg (43 μmol) scale based on **23a** with 18-C-6 (0.25 equiv.).

1.7 One-Pot Desilylative (4+4) Cyclodimerization

With optimized conditions for a one-pot desilylative nucleophilic (4+4) cyclodimerization reaction in hand, the scope was evaluated across fifteen other protected cyclopropenes **23** possessing different aryl substitution (**Table 8**).

Table 8. One-pot desilylative (4+4) cyclodimerization.

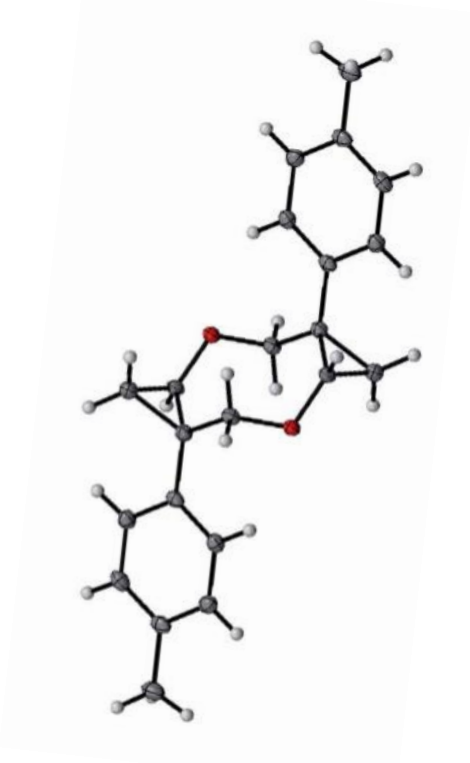


Dioxocanes **21a** through **21e** in **Table 8** allow for direct comparison of the one-pot desilylation/cyclization method to the stepwise protocol evaluated in **Table 4**. In all cases, the efficiency of nucleophilic (4+4) cyclodimerization remained essentially the same while avoiding the losses of material experienced in **Scheme 9**. All products were obtained as essentially a single diastereomer except for substrates possessing two fluorine substituents **21c** and **21j**, in which *cis*-configured dioxocanes **22c** and **22j** were observed in measurable quantities (**Table 8**).

1.8 Proposed Mechanism and Discussion of Diastereoselectivity

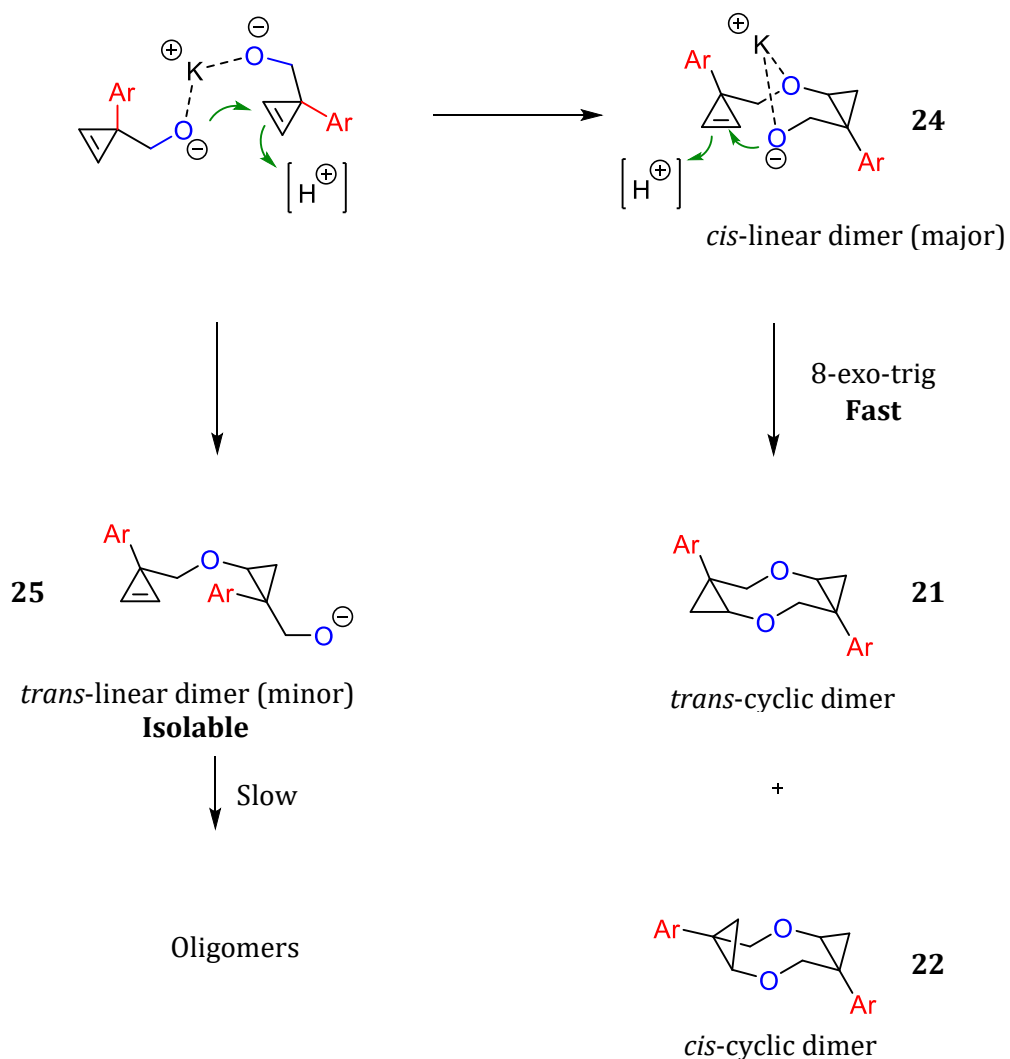
The stereochemical outcomes of the tricyclic products produced in **Table 8** were confirmed by X-ray analysis of 4-methyl substituted dioxocane **21g** (**Figure 3**), in which a *trans*-configuration is clearly seen with aryl substituents being placed on opposite faces of the 8-member-heterocycle.

Figure 3. ORTEP drawing of **21g** showing 50% probability amplitude displacement ellipsoids.



The high degree of *trans*-diastereoselectivity is believed to be rationalized by **Scheme 11**. The proposed mechanism begins with intermolecular nucleophilic attack of one alkoxide moiety on the less sterically hindered face of cyclopropene, possibly being assisted via coordination of the incoming nucleophile to a potassium cation, to establish *cis*-linear dimer **24**. From here, a subsequent 8-*exo-trig* strain-release driven nucleophilic addition occurs to produce *trans*-cyclic dimer **21** selectively, possibly once again aided by coordination of the alkoxide to potassium (**Scheme 11**).

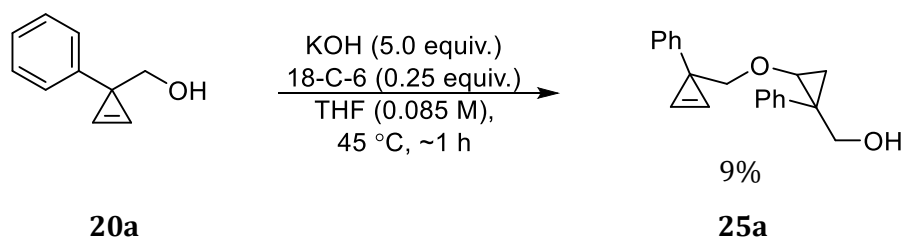
Scheme 11



The origin of diastereoselectivity during the intramolecular cyclization event is not precisely known, however, the formation of a more favorable transition state via participation of a potassium cation is believed to occur due to the deterioration of diastereoselectivity observed in reactions performed in polar cation coordinating solvents such as DMSO, DMA, and DMF (**Tables 3 and 7**).

A portion of the lost material balance can be accounted for by the formation of *trans*-linear dimer **25** which cannot undergo intramolecular cyclization due to the alkoxide moiety being oriented away from the site of ring closure. This species instead undergoes intermolecular nucleophilic attack to form various oligomers and polymers. At the optimized reaction concentration of 0.085 M, the intermolecular polymerization process occurs much slower than intramolecular cyclization, and by reduction of reaction temperature to 45 °C and careful monitoring of reaction progress it was possible to isolate and characterize **25a** in 9% yield (**Scheme 12**). The inability of the *trans*-linear dimer to undergo intramolecular cyclization was confirmed by subjecting **25a** to optimized conditions, from which, no evidence of the intended dioxocane was observed and only resulted in slow polymerization.

Scheme 12



1.9 Conclusion

In conclusion, a strain-release driven nucleophilic (4+4) cyclodimerization of cyclopropenes to provide a fused three ring system possessing a medium-sized eight member ring core was successfully developed. The process proceeds via face-selective nucleophilic attack of an alkoxide species on the strained double bond of cyclopropene followed by highly diastereoselective nucleophilic ring closure to provide interesting 1,5-dioxocane structures. The development of this process also resulted in an expedited and cost saving method of accessing prochiral cyclopropenes possessing an unsubstituted double bond via Rh(II)-catalyzed [2+1] cycloaddition reaction between TMS-acetylene and minimally purified diazoarylacetaes.

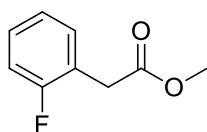
1.10 Experimental

1.10.1 General Information

NMR spectra were recorded on a Bruker Avance DPX-400 instrument, equipped with a quadruple-band gradient probe (H/C/P/F QNP) or a Bruker Avance DRX-500 with a dual carbon/proton cryoprobe (CPDUL). ^{13}C NMR spectra were registered with broadband decoupling. The (+) and (-) designations represent positive and negative intensities of signals in ^{13}C DEPT-135 experiments. IR spectra were recorded on a Shimadzu FT-IR 8400S instrument. HRMS was carried out on LCT Premier (Micromass Technologies) instrument; ESI TOF detection techniques were used. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph with FID detector and equipped with an AOC-20i auto-injector and an AOC-20S auto-sampler tray (150 vials); 30 m 0.25 mm 0.25 mm capillary column, SHR5XLB, polydimethylsiloxane; 5% Ph was employed. Helium (99.96%), additionally purified by passing consecutively through a CRS oxygen/moisture/hydrocarbon trap (#202839) and VICI oxygen/moisture trap (P100-1), was used as a carrier gas. Hydrogen gas was used as FID fuel; zero-grade air and zero-grade nitrogen were used as an oxidant and make-up gas, respectively, for the FID. All these gases were purified by passing through CRS #202839 traps. The following GC parameters were used for all analyses: carrier gas flow rate 2.5 mL/min; oven temperature program: 50 °C (2 min) – 20 °C/min – 230 °C (6 min), injector temperature 275 °C. HPLC analyses were performed on a Rainin Dynamax SD-200 equipped with Alltech Econosphere Si 5U column (L 150 mm ID 4.6 mm) or a 250 mm x 4.6 mm Chiracel OD-H column and Rainin Dynamax Absorbance detector UV-C set at 254 nm or Agilent Technologies 1220 Infinity system equipped with either Diacel Chirapak IC, Diacel Chirapak IE, or Diacel Chirapak IB. Glassware employed in moisture-free syntheses was flame-dried in vacuum prior to use. A combination of glove box and standard Schlenk technique was used to handle moisture sensitive materials. Column chromatography was carried out on silica

gel (Sorbent Technologies, 40-63 μm). Pre-coated silica gel plates (Sorbent Technologies Silica XG 200 μm) were used for TLC analyses. Anhydrous diethyl ether and THF were obtained by passing degassed commercially available HPLC-grade inhibitor-free solvents consecutively through two columns filled with activated alumina and stored over molecular sieves under nitrogen. Other anhydrous solvents were obtained according to standard procedures. Water was purified by dual stage deionization followed by dual stage reverse osmosis. Powdered potassium hydroxide was obtained by grinding commercially available pelleted reagent employing conventional electric-powered blade coffee-grinder housed inside a nitrogen-filled glove box. All other reagents were purchased from commercial vendors and used as received.

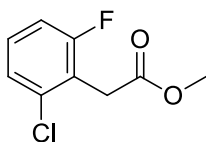
1.10.2 Esterification



methyl 2-(2-fluorophenyl)acetate (16p)

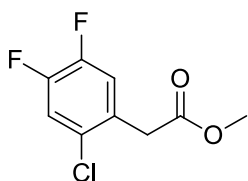
(Typical Esterification Procedure) 2-(2-fluorophenyl)acetic acid (9.69 g, 62.9 mmol, 1.0 equiv.) and amberlyst-15 exchange resin (100 mg) were combined in freshly distilled methanol (100 mL) and refluxed overnight with stirring. The solution was then filtered and concentrated under vacuum. The remaining solution was then added to cold water and extracted with ethyl acetate (3 x 30 mL). Combined organic layers were then washed successively with potassium carbonate and brine, dried with magnesium sulfate, and concentrated. If necessary, the product was then purified by column chromatography using a 3:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless oil in 73% yield (7.75 g, 46.1 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.33 – 7.21 (m, 2H), 7.16–7.00 (m, 2H), 3.71 (s, 3H), 3.68 (s, 2H); ^{13}C (126 MHz, CDCl_3): δ 171.2, 161.1 (d, J = 246.5 Hz), 131.5 (d, J = 4.0 Hz, +), 129.2 (d, J = 8.1 Hz, +), 124.2 (d, J = 3.7 Hz, +), 121.4 (d, J = 15.9 Hz), 115.5 (d, J = 21.6 Hz, +), 52.3 (+), 34.4 (d, J =

3.3 Hz, -); FTIR (KBr, cm^{-1}): 3032, 3001, 2955, 1744, 1620, 1587, 1495, 1458, 1435, 1418, 1344, 1285, 1258, 1234, 1209, 1163, 1100, 1013, 945, 930, 860, 835, 806, 758, 739, 685, 631; HRMS (TOF ES): Found 169.0668, calculated for $\text{C}_9\text{H}_{10}\text{FO}_2$ ($\text{M}+\text{H}$) 169.0665 (1.8 ppm).



methyl 2-(2-chloro-6-fluorophenyl)acetate (16h)

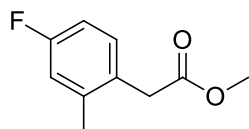
Titled compound was obtained via typical esterification procedure using 2-(2-chloro-6-fluorophenyl)acetic acid (20.0 g, 106.1 mmol, 1.0 equiv.), as a clear liquid in 73% yield (15.6 mg, 76.8 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.22 – 7.14 (m, 2H), 7.02 – 6.94 (m, 1H), 3.82 (s, 2H), 3.69 (s, 3H); ^{13}C (126 MHz, CDCl_3): δ 170.0, 161.5 (d, J = 248.8 Hz), 135.7 (d, J = 5.3 Hz), 129.1 (d, J = 9.5 Hz, +), 125.1 (d, J = 3.5 Hz, +), 121.0 (d, J = 18.6 Hz), 113.9 (d, J = 22.7 Hz, +), 52.2 (+), 31.7 (-); FTIR (KBr, cm^{-1}): 3001, 2953, 1747, 1609, 1580, 1466, 1454, 1435, 1416, 1340, 1292, 1248, 1221, 1171, 1138, 1065, 1014, 1003, 953, 897, 858, 827, 781, 746, 681, 660; HRMS (TOF ES): Found 203.0279, calculated for $\text{C}_9\text{H}_9\text{ClFO}_2$ ($\text{M}+\text{H}$) 203.0275 (2.0 ppm).



methyl 2-(2-chloro-4,5-difluorophenyl)acetate (16o)

Titled compound was obtained via typical esterification procedure using 2-(2-chloro-4,5-difluorophenyl)acetic acid (7.04 g, 34.1 mmol, 1.0 equiv.), as a pale yellow liquid in 80% yield (6.02 g, 27.3 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.23 (dd, J = 9.9, 7.2 Hz, 1H), 7.15 (dd, J = 10.5, 8.2 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 2H); ^{13}C (126 MHz, CDCl_3): δ 170.3, 149.3 (dd, J = 251.7, 13.6 Hz), 148.9 (dd, J = 248.9, 12.5 Hz), 129.2 (dd, J = 7.9, 3.7 Hz), 129.0 (dd, J = 5.9, 4.1 Hz), 119.8 (d, J = 19.0 Hz, +), 118.5 (d, J = 20.3 Hz, +), 52.4 (+), 38.1 (+); FTIR (KBr, cm^{-1}): 3057, 3003, 2957, 1747, 1732, 1607, 1504, 1437, 1421, 1402, 1340, 1302, 1263, 1198,

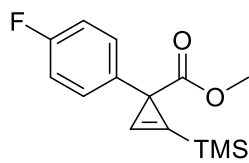
1165, 1151, 1018, 991, 939, 903, 876, 856, 822, 766, 721, 652; HRMS (TOF ES): Found 221.0183, calculated for $C_9H_8ClF_2O_2$ ($M+H$) 221.0181 (0.9 ppm).



methyl 2-(4-fluoro-2-methylphenyl)acetate (16q)

Titled compound was obtained via typical esterification procedure using 2-(4-fluoro-2-methylphenyl)acetic acid (10.7 g, 63.6 mmol, 1.0 equiv.), as a clear oil in 81% yield (9.38 g, 51.5 mmol); 1H NMR (400 MHz, $CDCl_3$): δ 7.15 (dd, J = 8.4, 5.8 Hz, 1H), 6.92 – 6.82 (m, 2H), 3.69 (s, 3H), 3.60 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.8, 162.0 (d, J = 245.1 Hz), 139.2 (d, J = 7.8 Hz), 131.6 (d, J = 8.2 Hz, +), 128.5 (d, J = 3.1 Hz), 117.0 (d, J = 21.3 Hz, +), 112.8 (d, J = 21.0 Hz, +), 52.0 (+), 38.2 (-), 19.7 (+); FTIR (KBr, cm^{-1}): 2995, 2953, 2928, 1730, 1610, 1591, 1501, 1435, 1381, 1339, 1313, 1256, 1211, 1161, 1095, 1005, 962, 924, 891, 864, 822, 793, 735, 723, 683, 617; HRMS (TOF ES): Found 182.0744, calculated for $C_{10}H_{11}FO_2$ ($M+$) 182.0743 (0.5 ppm).

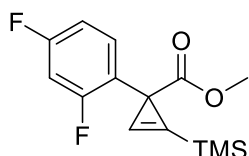
1.10.3 Rh(II)-Catalyzed Cyclopropenation



methyl 1-(4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18b)

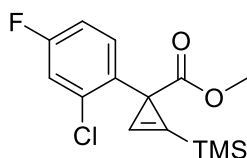
(Typical Cyclopropenation Procedure A) methyl 2-(4-fluorophenyl)acetate (**16b**) (5.0 g, 29.7 mmol, 1.0 equiv.) and tosyl azide (6.15 g, 31.2 mmol, 1.05 equiv.) were stirred in acetonitrile (75 mL) at 0 °C. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (5.45 g, 35.6 mmol, 1.2 equiv.) was then added drop wise to the stirring solution via an addition funnel. Upon complete addition, the reaction was allowed to warm to room temperature and was stirred overnight. Solvent was then evaporated and the reaction was partitioned between

saturated ammonium chloride and methylene chloride. The aqueous phase was then extracted with methylene chloride (3 x 30 mL). Combined organic phases were then washed with brine, dried with magnesium sulfate, filtered, and concentrated. The recovered material was then immediately filtered through a short pad of Silica gel using a 9:1 mixture of hexane and ethyl acetate. methyl 2-diazo-2-(4-fluorophenyl)acetate was obtained as an orange oil in 62% crude yield (3.6 g, 18.5 mmol). methyl 2-diazo-2-(4-fluorophenyl)acetate (3.60 g, 18.5 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~4.0 mL) and added via syringe pump over 18 hours to a stirring and refluxing suspension of rhodium(II) acetate dimer catalyst (3.7 mg, 8.30 μ mol, 0.09 mol%) in trimethylsilylacetylene (26 mL, 185 mmol, 10.0 equiv.). After complete addition, the reaction was monitored by gas chromatography until complete consumption of the starting material was observed. Once this was achieved, the reflux condenser was replaced with distillation head and most of the trimethylsilylacetylene was recovered by distillation at ambient pressure. Residual solvent was then removed under vacuum. The reaction was then purified by column chromatography using a 3:1 hexanes:methylene chloride mobile phase. The titled compound was obtained as an amber oil in 74% yield (3.64 g, 13.8 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.23 (s, 1H), 7.06-7.01 (m, 2H), 6.79-6.73 (m, 2H), 3.47 (s, 3H), 0.00 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 176.0, 161.3 (d, J = 244.4 Hz), 138.3 (d, J = 3.2 Hz), 130.0 (d, J = 7.9 Hz, 2C, +), 120.3, 115.5 (+), 114.8 (d, J = 21.3 Hz, 2C, +), 52.0 (+), 30.7, -1.4 (3C, +); FTIR (KBr, cm^{-1}): 3119, 3042, 2993, 2955, 2901, 1732, 1703, 1603, 1510, 1435, 1286, 1252, 1223, 1157, 1034, 1014, 897, 847, 820, 760, 710; HRMS (TOF ES): Found 301.1036, calculated for $\text{C}_{15}\text{H}_{19}\text{FO}_2\text{SiNa}$ ($\text{M}+\text{Na}$) 301.1036 (0.0 ppm).



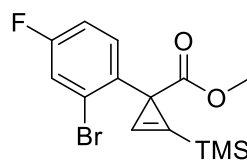
methyl 1-(2,4-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18c)

Compound was obtained via typical cyclopropenation procedure A using methyl 2-(2,4-difluorophenyl)acetate (**16c**) (6.83 g, 36.7 mmol, 1.0 equiv.), tosyl azide (7.60 g, 38.5 mmol, 1.05 equiv.), acetonitrile (105 mL), and DBU (6.70 g, 44.0 mmol, 1.20 equiv.). methyl 2-diazo-2-(2,4-difluorophenyl)acetate was obtained as a orange liquid in 83% yield (6.49 g, 30.59 mmol). methyl 2-diazo-2-(2,4-difluorophenyl)acetate (6.49 g, 30.6 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~7.5 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (6.08 mg, 13.8 μ mol, 0.09 mol%) in trimethylsilylacetylene (43.5 mL, 306 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 71% yield (6.1 g, 21.6 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.50 (s, 1H), 7.08-7.01 (m, 1H), 6.83 – 6.71 (m, 2H), 3.64 (s, 3H), 0.21 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 175.7, 162.0 (dd, J = 246.3, 8.8 Hz), 161.9 (dd, J = 246.3, 9.5 Hz), 131.0 (dd, J = 9.6, 5.9 Hz, +), 126.4 (dd, J = 16.0, 3.9 Hz), 121.4, 115.9 (+), 111.0 (dd, J = 21.1, 3.7 Hz, +), 103.8 (t, J = 25.7 Hz, +), 52.3 (+), 26.7, -1.6 (3C, +); FTIR (KBr, cm^{-1}): 3124, 3078, 2995, 2957, 2903, 1736, 1730, 1701, 1612, 1601, 1502, 1425, 1290, 1269, 1252, 1227, 1211, 1163, 1138, 1111, 1090, 1030, 1013, 964, 845, 785, 760, 712, 615; HRMS (TOF ES): Found 282.0888, calculated for $\text{C}_{14}\text{H}_{16}\text{F}_2\text{O}_2\text{Si}$ (M^+) 282.0888 (0.0 ppm).



methyl 1-(2-chloro-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18d)

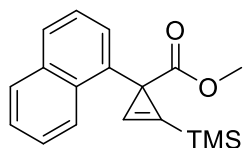
Compound was obtained via typical cyclopropenation procedure A using methyl 2-(2-chloro-4-fluorophenyl)acetate (**16d**) (5.0 g, 24.7 mmol, 1.0 equiv.), tosyl azide (5.11 g, 25.9 mmol, 1.05 equiv.), acetonitrile (70.9 mL), and DBU (4.51 g, 29.6 mmol, 1.2 equiv.). methyl 2-(2-chloro-4-fluorophenyl)-2-diazoacetate was obtained as an orange liquid in 88% yield (4.96 g, 21.7 mmol). methyl 2-(2-chloro-4-fluorophenyl)-2-diazoacetate (4.96 g, 21.7 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~5.0 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (4.30 mg, 9.76 μ mol, 0.09 mol%) in trimethylsilylacetylene (31.0 mL, 217 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 49% yield (3.2 g, 10.7 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.57 (s, 1H), 7.12 – 7.06 (m, 2H), 6.91 (td, J = 8.3, 2.6 Hz, 1H), 3.64 (s, 3H), 0.25 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 175.5, 161.4 (d, J = 248.4 Hz), 137.1 (d, J = 3.6 Hz), 135.9 (d, J = 10.4 Hz), 131.4 (d, J = 8.8 Hz, +), 121.9, 117.8 (+), 116.8 (d, J = 24.6 Hz, +), 114.1 (d, J = 21.0 Hz, +), 52.4 (+), 31.0, -1.3 (3C, +); FTIR (KBr, cm^{-1}): 3123, 3072, 2955, 2901, 2847, 1929, 1753, 1730, 1693, 1599, 1587, 1487, 1435, 1393, 1319, 1281, 1254, 1221, 1051, 1009, 916, 891, 847, 710, 604; HRMS (TOF ES): Found 299.0672, calculated for $\text{C}_{14}\text{H}_{17}\text{ClFO}_2\text{Si}$ ($\text{M}+\text{H}$) 299.0670 (0.7 ppm).



methyl 1-(2-bromo-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18e)

Compound was obtained via typical cyclopropenation procedure A using methyl 2-(2-bromo-4-fluorophenyl)acetate (**16e**) (15.3 g, 61.9 mmol, 1.0 equiv.), tosyl azide (12.8 g, 65.0 mmol, 1.05 equiv.), acetonitrile (178 mL), and DBU (11.3 g, 74.3 mmol, 1.20 equiv.). methyl 2-(2-bromo-4-fluorophenyl)-2-diazoacetate was obtained as a orange liquid in 71% yield

(12.0 g, 44.1 mmol). methyl 2-(2-bromo-4-fluorophenyl)-2-diazoacetate (12.0 g, 43.9 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~11.0 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (8.70 mg, 19.8 μ mol, 0.09 mol%) in trimethylsilylacetylene (62.6 mL, 439.4 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 68% yield (10.2 g, 29.7 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.61 (s, 1H), 7.27 (dd, J = 2.5, 1.25 Hz, 1H) 7.09 (dd, J = 8.5, 6.0 Hz, 1H), 6.96 (td, J = 8.3, 2.7 Hz, 1H), 3.64 (s, 3H), 0.27 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 175.4, 161.2 (d, J = 249.7 Hz), 138.8 (d, J = 3.5 Hz), 131.5 (d, J = 8.5 Hz, +), 125.6 (d, J = 9.6 Hz), 121.9, 120.0 (d, J = 24.3 Hz, +), 118.6 (+), 114.7 (d, J = 20.9 Hz, +), 52.4 (+), 33.2, -1.2 (3C, +); FTIR (KBr, cm^{-1}): 3123, 3069, 2953, 2901, 2841, 1730, 1697, 1597, 1580, 1485, 1433, 1416, 1385, 1279, 1252, 1219, 1105, 1041, 1009, 968, 897, 847, 781, 760, 712, 673, 638, 604; HRMS (TOF ES): Found 343.0168, calculated for $\text{C}_{14}\text{H}_{17}\text{BrFO}_2\text{Si}$ (M+H) 343.0165 (0.9 ppm).

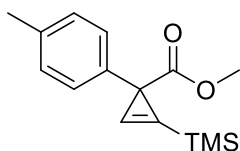


methyl 1-(naphthalen-1-yl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18f)

(Typical Cyclopropenation Procedure B)

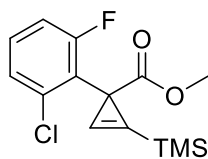
methyl 2-(naphthalen-1-yl)acetate (**16f**) (22.0 g, 110.0 mmol, 1.0 equiv.) and tosyl azide (22.8 g, 115.6 mmol, 1.05 equiv.) were stirred in acetonitrile (250 mL) at 0 $^{\circ}\text{C}$. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (20.1 g, 132.1 mmol, 1.2 equiv.) was then added drop wise to the stirring solution via an addition funnel. Upon complete addition, the reaction was allowed to warm to room temperature and was stirred overnight. Solvent was then evaporated and the reaction was partitioned between saturated ammonium chloride and methylene chloride. The aqueous phase was then extracted with methylene chloride (3 x 30 mL). Combined organic phases were then washed with brine, dried with magnesium sulfate, filtered, and concentrated.

The recovered material was then immediately filtered through a short pad of Silica gel using a 9:1 mixture of hexane and ethyl acetate. methyl 2-diazo-2-(naphthalen-1-yl)acetate was obtained as a red solid in 65% crude yield (16.2 g, 72.0 mmol). An apparatus was then assembled consisting of a round bottom flask topped with an addition funnel and a small water cooled condenser. methyl 2-diazo-2-(naphthalen-1-yl)acetate (4.65 g, 20.5 mmol, 1.0 equiv.), as a solid, was then rolled into a conical piece of filter paper and placed within the addition funnel. The round bottom flask, containing rhodium(II) acetate dimer catalyst (4.0 mg, 9.2 μ mol, 0.09 mol%) in trimethylsilylacetylene (29.0 mL, 205 mmol, 10.0 equiv.) was then placed in an oil bath and heated until reflux was achieved at a rate in which condensation occurred just within the addition funnel. This state of reflux was maintained until GC analysis showed complete conversion of the starting material, then the addition funnel was replaced with a distillation head and excess trimethylsilylacetylene was distilled under ambient pressure. The reaction was then purified by column chromatography using a 3:1 hexanes:methylene chloride mobile phase. The titled compound was obtained as a brown oil in 73% yield (2.16 g, 7.29 mmol); ^1H NMR (400 MHz, CDCl_3): δ 8.13 – 8.08 (m, 1H), 7.89-7.84 (m, 1H), 7.81 (s, 1H), 7.78-7.74 (m, 1H), 7.57 – 7.39 (m, 3H), 7.34-7.29 (m, 1H), 3.60 (s, 3H), 0.27 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 177.0 139.8, 133.9, 132.6, 128.8 (+), 127.6 (+), 126.2 (+), 125.9 (+), 125.8 (+), 125.7 (+), 124.8 (+), 121.9, 119.6 (+), 52.4 (+), 30.8, -1.1 (3C, +); FTIR (KBr, cm^{-1}): 3119, 3059, 3043, 3011, 2953, 2899, 1927, 1730, 1697, 1595, 1508, 1433, 1394, 1340, 1283, 1250, 1221, 1177, 1144, 1121, 1080, 1049, 1020, 1001, 951, 893, 843, 802, 777, 762, 735, 708, 667, 642, 631; HRMS (TOF ES): Found 296.1233, calculated for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Si}$ (M^+) 296.1233 (0.0 ppm).



methyl 1-(p-tolyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18g)

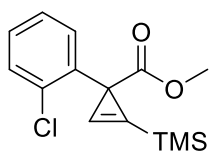
Compound was obtained via typical cyclopropenation procedure B using methyl 2-(p-tolyl)acetate (**16g**) (9.3 g, 56.6 mmol, 1.0 equiv.), tosyl azide (11.7 g, 59.5 mmol, 1.05 equiv.), acetonitrile (162 mL), and DBU (10.3 g, 67.9 mmol, 1.20 equiv.). methyl 2-diazo-2-(p-tolyl)acetate was obtained as a red solid in 47% crude yield (5.06 g, 26.6 mmol). Subsequent operations were performed with methyl 2-diazo-2-(p-tolyl)acetate (2.0 g, 10.5 mmol, 1.0 equiv.), rhodium(II) acetate dimer (2.10 mg, 4.73 μ mol, 0.09 mol%) and trimethylsilylacetylene (15.0 mL, 105 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 71% yield (1.93 g, 7.41 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.45 (s, 1H), 7.16 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 3.68 (s, 3H), 2.32 (s, 3H), 0.21 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 176.4, 139.5, 135.7, 128.8 (2C, +), 128.3 (2C, +), 120.1, 116.2, 52.0 (+), 31.2 (+), 21.2 (+), -1.3 (3C, +); FTIR (KBr, cm^{-1}): 3117, 3022, 2993, 2953, 2922, 2901, 2870, 1730, 1703, 1605, 1514, 1433, 1412, 1379, 1327, 1288, 1250, 1219, 1207, 1182, 1117, 1095, 1036, 1016, 970, 897, 845, 768, 719, 708, 635; HRMS (TOF ES): Found 261.1311, calculated for $\text{C}_{15}\text{H}_{21}\text{O}_2\text{Si}$ ($\text{M}+\text{H}$) 261.1311 (0.0 ppm).



methyl 1-(2-chloro-6-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18h)

Compound was obtained via typical cyclopropenation procedure A using methyl 2-(2-chloro-6-fluorophenyl)acetate (**16h**) (6.51 g, 32.1 mmol, 1.0 equiv.), tosyl azide (6.65 g, 33.7 mmol, 1.05 equiv.), acetonitrile (93 mL), and DBU (5.87 g, 38.6 mmol, 1.20 equiv.). methyl 2-(2-chloro-6-fluorophenyl)-2-diazoacetate was obtained as a yellow liquid in 48% yield (3.55 g, 15.53 mmol). methyl 2-(2-chloro-6-fluorophenyl)-2-diazoacetate (2.7 g, 11.8 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (\sim 2.5 mL) and added

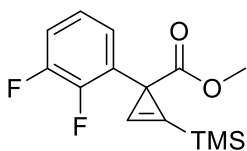
to a refluxing suspension of rhodium(II) acetate dimer catalyst (2.3 mg, 5.30 μmol , 0.09 mol%) in trimethylsilylacetylene (16.8 mL, 118 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 43% yield (1.50 g, 5.02 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, J = 2.3 Hz, 1H), 7.19 – 7.09 (m, 2H), 7.00 – 6.89 (m, 1H), 3.64 (s, 3H), 0.23 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 175.3, 162.5 (d, J = 248.0 Hz), 136.3 (d, J = 5.3 Hz), 129.0 (d, J = 17.6 Hz), 128.7 (d, J = 9.8 Hz, +), 125.3 (d, J = 3.4 Hz, +), 119.4 (d, J = 2.1 Hz), 117.8 (d, J = 3.3 Hz, +), 114.2 (d, J = 23.1 Hz, +), 52.4 (+), 25.9 (d, J = 2.0 Hz), -1.5 (3C, +); FTIR (KBr, cm^{-1}): 2955, 2903, 1734, 1705, 1607, 1572, 1447, 1435, 1418, 1252, 1242, 1217, 1177, 1146, 1030, 1011, 885, 845, 795, 781, 760, 721, 636; HRMS (TOF ES): Found 297.0517, calculated for $\text{C}_{14}\text{H}_{15}\text{ClFO}_2\text{Si}$ (M-H) 297.0514 (1.0 ppm).



methyl 1-(2-chlorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18i)

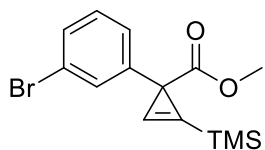
Compound was obtained via typical cyclopropanation procedure A using methyl 2-(2-chlorophenyl)acetate (**16i**) (5.89 g, 31.9 mmol, 1.0 equiv.), tosyl azide (6.80 g, 33.5 mmol, 1.05 equiv.), acetonitrile (92 mL), and DBU (5.82 g, 38.3 mmol, 1.2 equiv.). methyl 2-(2-chlorophenyl)-2-diazoacetate was obtained as a orange liquid in 83% yield (5.55 g, 26.4 mmol). methyl 2-(2-chlorophenyl)-2-diazoacetate (5.55 g, 26.4 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~5.0 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (5.2 mg, 11.9 μmol , 0.09 mol%) in trimethylsilylacetylene (37.5 mL, 263 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 64% yield (4.75 g, 16.9 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.61 (s, 1H), 7.33 (dd, J = 7.6, 1.6 Hz, 1H), 7.22 – 7.11 (m, 3H), 3.64 (s, 3H), 0.27 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 175.6, 140.9, 135.2, 130.3 (+), 129.4 (+), 128.1 (+), 126.9 (+), 121.8, 118.0 (+), 52.2 (+), 31.5, -1.3 (3C, +); FTIR (KBr, cm^{-1}): 3123, 3061, 3020, 2953, 2901, 2841, 2405, 2253, 1950, 1736, 1591, 1433, 1414, 1209, 1059, 1038,

1024, 1011, 893, 847, 750, 735, 717, 700, 642; HRMS (TOF ES): Found 287.0846, calculated for $C_{14}H_{17}ClO_2SiLi$ (M+Li) 287.0846 (0.0 ppm).



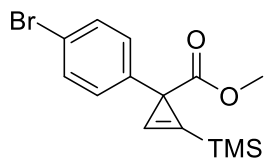
methyl 1-(2,3-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18j)

Compound was obtained via typical cyclopropanation procedure A using methyl 2-(2,3-difluorophenyl)acetate (**16j**) (6.4 g, 34.38 mmol, 1.0 equiv.), tosyl azide (7.12 g, 36.1 mmol, 1.05 equiv.), acetonitrile (99 mL), and DBU (6.28 g, 41.25 mmol, 1.20 equiv.). methyl 2-diazo-2-(2,3-difluorophenyl)acetate was obtained as a orange liquid in 77% yield (5.60 g, 26.4 mmol). methyl 2-diazo-2-(2,3-difluorophenyl)acetate (5.60 g, 26.4 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~5.0 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (5.30 mg, 11.9 μ mol, 0.09 mol%) in trimethylsilylacetylene (37.6 mL, 264 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 74% yield (5.55 g, 19.7 mmol); 1H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 1H), 7.04 – 6.92 (m, 2H), 6.86-6.81 (m, 1H), 3.63 (s, 3H), 0.22 (s, 9H); ^{13}C (126 MHz, $CDCl_3$): δ 175.3, 150.5 (dd, $J=247.7$, 13.1 Hz), 149.8 (dd, $J=247.2$, 12.4 Hz) 132.8 (d, $J=12.4$ Hz), 124.9 (t, $J=3.1$ Hz, +), 123.8 (dd, $J=7.0$, 4.6 Hz, +), 121.1, 115.8 (+), 115.7 (d, $J=17.3$ Hz, +), 52.3 (d, $J=1.7$ Hz, +), 27.0 (t, $J=2.4$ Hz), -1.7 (3C, +); FTIR (KBr, cm^{-1}): 3124, 3036, 2957, 2903, 2843, 1730, 1703, 1624, 1591, 1479, 1435, 1302, 1288, 1252, 1229, 1215, 1163, 1051, 993, 874, 845, 818, 789, 762, 725, 710, 640, 615. HRMS (TOF ES): Found 283.0965, calculated for $C_{14}H_{17}F_2O_2Si$ (M+H) 283.0966 (0.4 ppm).



methyl 1-(3-bromophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18k)

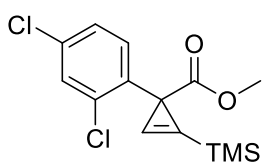
Compound was obtained via typical cyclopropanation procedure A using methyl 2-(3-bromophenyl)acetate (**16k**) (2.75 g, 12.0 mmol, 1.0 equiv.), tosyl azide (2.48 g, 12.6 mmol, 1.05 equiv.), acetonitrile (35 mL), and DBU (2.19 g, 14.4 mmol, 1.20 equiv.). methyl 2-(3-bromophenyl)-2-diazoacetate was obtained as a orange liquid in 65% yield (2.0 g, 7.84 mmol). methyl 2-(3-bromophenyl)-2-diazoacetate (2.0 g, 7.84 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~2.5 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (1.56 mg, 3.5 μ mol, 0.09 mol%) in trimethylsilylacetylene (11.2 mL, 78.4 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 59% yield (1.5 g, 4.61 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.41-7.39 (m, 1H), 7.39 (s, 1H), 7.31-7.28 (m, 1H), 7.24-7.21 (m, 1H), 7.13 (t, J = 7.8 Hz, 1H), 3.67 (s, 3H), 0.20 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 175.4, 145.0, 131.4 (+), 129.5 (+), 129.1 (+), 127.1 (+), 122.1, 119.6, 115.2 (+), 52.1 (+), 31.0, -1.4 (3C, +); FTIR (KBr, cm^{-1}): 3121, 3063, 2953, 2899, 2841, 1732, 1705, 1593, 1562, 1474, 1435, 1416, 1283, 1252, 1209, 1107, 1072, 1036, 1014, 997, 974, 845, 781, 760, 723, 694, 633; HRMS (TOF ES): Found 324.0181, calculated for $\text{C}_{14}\text{H}_{17}\text{BrO}_2\text{Si}$ (M^+) 324.0181 (0.0 ppm).



methyl 1-(4-bromophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18l)

Compound was obtained via typical cyclopropanation procedure A using methyl 2-(4-bromophenyl)acetate (**16l**) (2.70 g, 11.8 mmol, 1.0 equiv.), tosyl azide (2.44 g, 12.4 mmol, 1.05 equiv.), acetonitrile (34.0 mL), and DBU (2.15 g, 14.1 mmol, 1.20 equiv.). methyl 2-(4-bromophenyl)-2-diazoacetate was obtained as a orange liquid in 89% yield (2.67 g, 10.5 mmol). methyl 2-(4-bromophenyl)-2-diazoacetate (2.67 g, 10.5 mmol, 1.0 equiv.) was then dissolved in

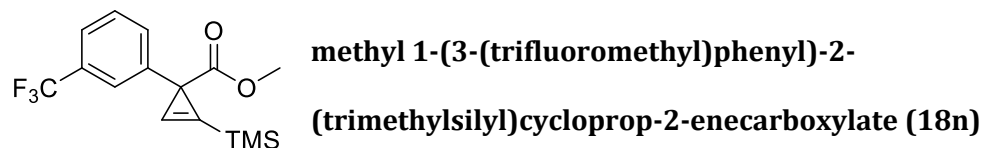
a minimum amount of trimethylsilylacetylene (~2.5 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (2.08 mg, 4.71 μ mol, 0.09 mol%) in trimethylsilylacetylene (14.9 mL, 105 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 72% yield (2.45 g, 7.53 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.40 (s, 1H), 7.38 (d, J = 5.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 3.66 (s, 3H), 0.19 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 175.7, 141.7, 131.0 (2C, +), 130.2 (2C, +), 120.0, 119.9, 115.1 (+), 52.1 (+), 30.9, -1.4 (3C, +); FTIR (KBr, cm^{-1}): 3121, 3080, 3063, 3024, 2953, 2899, 2841, 1730, 1703, 1589, 1487, 1433, 1394, 1288, 1252, 1209, 1111, 1072, 1032, 1009, 897, 845, 789, 760, 721, 679, 636; HRMS (TOF ES): Found 342.0536, calculated for $\text{C}_{14}\text{H}_{21}\text{BrO}_2\text{SiNH}_4$ ($\text{M}+\text{NH}_4$) 342.0525 (3.2 ppm).



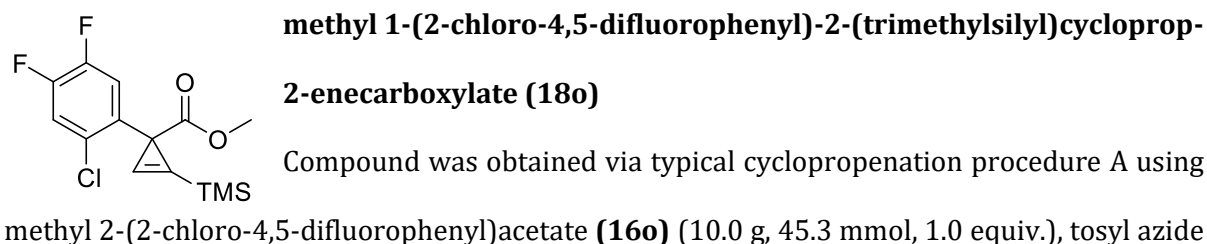
methyl 1-(2,4-dichlorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18m)

Compound was obtained via typical cyclopropanation procedure A using methyl 2-(2,4-dichlorophenyl)acetate (**16m**) (8.75 g, 39.9 mmol, 1.0 equiv.), tosyl azide (8.27 g, 41.9 mmol, 1.05 equiv.), acetonitrile (115 mL), and DBU (7.30 g, 47.9 mmol, 1.20 equiv.). methyl 2-diazo-2-(2,4-dichlorophenyl)acetate was obtained as an orange liquid in 79% yield (7.69 g, 31.38 mmol). methyl 2-diazo-2-(2,4-dichlorophenyl)acetate (7.69 g, 31.4 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~7.5 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (6.20 mg, 14.1 μ mol, 0.09 mol%) in trimethylsilylacetylene (44.7 mL, 314 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 46% yield (4.5 g, 14.3 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.57 (s, 1H), 7.35 (d, J = 2.1 Hz, 1H), 7.17 (dd, J = 8.2, 2.1 Hz, 1H), 7.05 (d, J = 8.2 Hz, 1H), 3.64 (s, 3H), 0.25 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 175.3, 139.8, 136.0, 133.1, 131.3 (+), 129.3 (+), 127.3 (+), 121.9, 117.6 (+), 52.4 (+), 31.1, -1.3 (3C, +); FTIR (KBr, cm^{-1}): 3123, 2953, 2901, 1736, 1701, 1587, 1556, 1472, 1433,

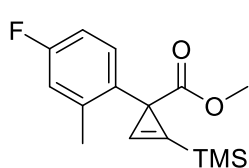
1377, 1283, 1250, 1217, 1101, 1059, 1024, 1011, 966, 897, 847, 812, 766, 710, 636; HRMS (TOF ES): Found 321.0463, calculated for $C_{14}H_{16}Cl_2O_2SiLi$ (M+Li) 321.0457 (1.9 ppm).



Compound was obtained via typical cyclopropanation procedure A using methyl 2-(3-(trifluoromethyl)phenyl)acetate (**16n**) (3.70 g, 17.0 mmol, 1.0 equiv.), tosyl azide (3.51 g, 17.8 mmol, 1.05 equiv.), acetonitrile (49.0 mL), and DBU (3.10 g, 20.4 mmol, 1.20 equiv.). methyl 2-diazo-2-(3-(trifluoromethyl)phenyl)acetate was obtained as a orange liquid in 95% yield (3.95 g, 16.18 mmol). methyl 2-diazo-2-(3-(trifluoromethyl)phenyl)acetate (3.95 g, 16.2 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~3.5 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (3.20 mg, 7.28 μ mol, 0.09 mol%) in trimethylsilylacetylene (23.0 mL, 162 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 64% yield (3.25 g, 10.3 mmol); 1H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.43 (m, 3H), 7.42 (s, 1H), 7.41 – 7.35 (m, 1H), 3.68 (s, 3H), 0.20 (s, 9H); ^{13}C (126 MHz, $CDCl_3$): δ 175.4, 143.7, 132.0 (d, J = 1.4 Hz, +), 130.3 (q, J = 31.9 Hz), 128.4 (+), 125.1 (d, J = 3.8 Hz, +), 124.4 (q, J = 272.3), 122.9 (d, J = 3.8 Hz, +), 119.5, 115.2 (+), 52.1 (+), 31.1, -1.5 (3C, +); FTIR (KBr, cm^{-1}): 2957, 1734, 1705, 1491, 1437, 1333, 1275, 1254, 1207, 1165, 1124, 1074, 1038, 845, 802, 762, 702. HRMS (TOF ES): Found 315.1027, calculated for $C_{15}H_{18}F_3O_2Si$ (M+H) 315.1028 (0.3 ppm).



(9.39 g, 47.6 mmol, 1.05 equiv.), acetonitrile (130 mL), and DBU (8.28 g, 54.4 mmol, 1.20 equiv.). methyl 2-(2-chloro-4,5-difluorophenyl)-2-diazoacetate was obtained as a orange oil in 92% yield (10.3 g, 41.6 mmol). methyl 2-(2-chloro-4,5-difluorophenyl)-2-diazoacetate (10.3 g, 41.6 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~11.0 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (8.27 mg, 18.7 μ mol, 0.09 mol%) in trimethylsilylacetylene (59.2 mL, 416 mmol, 10.0 equiv.). The titled compound was obtained as a brown oil in 52% yield (6.9 g, 21.8 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.54 (s, 1H), 7.17 (dd, J = 9.9, 7.2 Hz, 1H), 6.92 (dd, J = 10.6, 8.2 Hz, 1H), 3.65 (s, 3H), 0.25 (d, J = 0.6 Hz, 9H); ^{13}C (126 MHz, CDCl_3): δ 175.0, 149.1 (dd, J = 247.5, 3.7 Hz), 149.0 (dd, J = 248.8, 4.8 Hz), 138.1 (t, J = 4.5 Hz), 129.9 (dd, J = 7.9, 3.4 Hz), 121.9, 118.8 (d, J = 18.1 Hz, +), 118.5 (d, J = 20.2 Hz, +), 117.4 (+), 52.4 (+), 31.1, -1.3 (3C, +); FTIR (KBr, cm^{-1}): 3123, 3051, 2955, 2903, 2843, 2359, 1732, 1703, 1601, 1495, 1460, 1435, 1396, 1308, 1252, 1219, 1200, 1165, 1105, 1057, 997, 966, 910, 878, 847, 804, 768, 712, 660, 633, 619; HRMS (TOF ES): Found 339.0397, calculated for $\text{C}_{14}\text{H}_{15}\text{ClF}_2\text{O}_2\text{SiNa}$ ($\text{M}+\text{Na}$) 339.0396 (0.3 ppm).

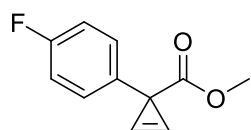


methyl 1-(4-fluoro-2-methylphenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (18q)

Compound was obtained via typical cyclopropenation procedure A using methyl 2-(4-fluoro-2-methylphenyl)acetate (**16q**) (2.38 g, 29.5 mmol, 1.0 equiv.), tosyl azide (6.11 g, 31.0 mmol, 1.05 equiv.), acetonitrile (84 mL), and DBU (5.39 g, 35.4 mmol, 1.20 equiv.). methyl 2-diazo-2-(4-fluoro-2-methylphenyl)acetate was obtained as a orange oil in 86% yield (5.3 g, 25.5 mmol). methyl 2-diazo-2-(4-fluoro-2-methylphenyl)acetate (2.0 g, 9.60 mmol, 1.0 equiv.) was then dissolved in a minimum amount of trimethylsilylacetylene (~2.5 mL) and added to a refluxing suspension of rhodium(II) acetate dimer catalyst (1.9 mg, 4.3 μ mol, 0.09 mol%) in

trimethylsilylacetylene (13.7 mL, 96.0 mmol, 10.0 equiv.). The titled compound was obtained as a yellow oil in 35% yield (0.94 g, 3.38 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.62 (s, 1H), 7.01 (dd, J = 8.4, 5.9 Hz, 1H), 6.88 – 6.76 (m, 2H), 3.64 (s, 3H), 2.33 (s, 3H), 0.27 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 176.4, 161.6 (d, J = 244.3 Hz), 139.9 (d, J = 7.9 Hz), 137.2 (d, J = 3.2 Hz), 130.4 (d, J = 8.4 Hz, +), 121.6, 119.5 (+), 116.8 (d, J = 21.0 Hz, +), 112.7 7(d, J = 21.0 Hz, +), 52.3 (+), 30.7, 19.7 (d, J = 1.7 Hz, +), -1.2 (3C, +); FTIR (KBr, cm^{-1}): 3119, 2955, 2928, 2901, 2091, 1730, 1697, 1614, 1587, 1495, 1435, 1412, 1377, 1269, 1252, 1229, 1151, 1109, 1090, 1030, 1011, 972, 953, 928, 885, 845, 781, 760, 729, 710, 640, 604; HRMS (TOF ES): Found 301.1036, calculated for $\text{C}_{15}\text{H}_{19}\text{FO}_2\text{SiNa}$ ($\text{M}+\text{Na}$) 301.1036 (0.0 ppm).

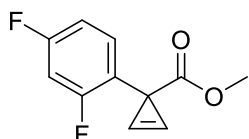
1.10.4 Cyclopropene Desilylation



methyl 1-(4-fluorophenyl)cycloprop-2-enecarboxylate (19b)

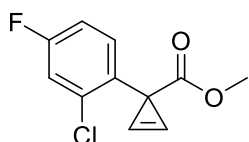
(Typical Desilylation Procedure) methyl 1-(4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18b**) (1.06 mg, 4.0 mmol, 1.0 equiv.) was dissolved in THF (6.50 mL) at 0 °C and 10% aqueous potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.) was added drop wise. Upon complete addition, the reaction was allowed to warm to room temperature and stirred until gas chromatography showed complete conversion of starting material. Ether (20 mL) and brine (25 mL) were added to the solution and the aqueous layer was extracted (3 x 10 mL). The combined organic layers were then washed with brine (20 mL), dried with magnesium sulfate, filtered, and concentrated. The product was then purified by column chromatography using 6:1 Hexane:ethyl acetate as the mobile phase to provide the titled compound as a very pale yellow oil in 84% yield (648 mg, 3.36 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.25 – 7.20 (m, 2H), 7.20 (s, 2H), 7.03 – 6.95 (m, 2H), 3.70 (s, 3H); ^{13}C (126 MHz, CDCl_3): δ 175.5,

161.7 (d, $J = 245.2$ Hz), 137.4 (d, $J = 3.2$ Hz), 130.0 (d, $J = 8.1$ Hz, 2C, +), 115.1 (d, $J = 21.4$ Hz, 2C, +), 107.8 (2C, +), 52.5 (+), 30.1; FTIR (KBr, cm^{-1}): 3159, 3117, 3042, 2999, 2953, 1720, 1659, 1603, 1510, 1435, 1292, 1267, 1225, 1161, 1109, 1095, 1030, 1005, 899, 870, 831, 818, 777, 744, 625; HRMS (TOF ES): Found 215.0485, calculated for $\text{C}_{11}\text{H}_9\text{O}_2\text{FNa}$ ($\text{M}+\text{Na}$) 215.0484 (0.5 ppm).



methyl 1-(2,4-difluorophenyl)cycloprop-2-enecarboxylate (19c)

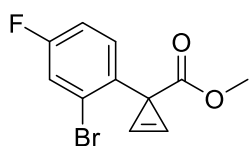
Compound was obtained via typical desilylation procedure using methyl 1-(2,4-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18c**) (1.13 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 86% yield (723 mg, 3.44 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.27 (s, 2H), 7.10 (td, $J = 8.5, 6.4$ Hz, 1H), 6.85 – 6.72 (m, 2H), 3.67 (s, 3H); ^{13}C (126 MHz, CDCl_3): δ 175.1, 162.2 (dd, $J = 247.8, 11.9$ Hz), 161.8 (dd, $J = 249.0, 12.0$ Hz), 130.9 (dd, $J = 9.6, 5.8$ Hz, +), 125.4 (dd, $J = 15.9, 3.9$ Hz), 111.2 (dd, $J = 21.1, 3.8$ Hz, +), 108.0 (d, $J = 1.5$ Hz, 2C, +), 104.0 (t, $J = 25.5$ Hz, +), 52.7 (+), 25.9 (d, $J = 1.4$ Hz); FTIR (KBr, cm^{-1}): 3165, 3123, 2955, 1720, 1664, 1612, 1599, 1501, 1423, 1292, 1269, 1244, 1213, 1140, 1092, 1026, 1007, 968, 939, 878, 851, 785, 748, 628, 613; HRMS (TOF ES): Found 209.0413, calculated for $\text{C}_{11}\text{H}_7\text{O}_2\text{F}_2$ ($\text{M}-\text{H}$) 209.0414 (0.5 ppm).



methyl 1-(2-chloro-4-fluorophenyl)cycloprop-2-enecarboxylate (19d)

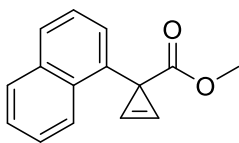
Compound was obtained via typical desilylation procedure using methyl 1-(2-bromo-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18d**) (1.19 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 80% yield (729 mg, 3.22 mmol);

^1H NMR (400 MHz, CDCl_3): δ 7.31 (s, 2H), 7.16 (dd, J = 8.5, 6.0 Hz, 1H), 7.09 (dd, J = 8.5, 2.6 Hz, 1H), 6.93 (td, J = 8.3, 2.6 Hz, 1H), 3.67 (s, 3H); ^{13}C (126 MHz, CDCl_3): δ 175.1, 161.7 (d, J = 248.9 Hz), 136.2 (d, J = 3.7 Hz), 135.8 (d, J = 10.4 Hz), 131.2 (d, J = 9.0 Hz, +), 116.9 (d, J = 24.8 Hz, +), 114.3 (d, J = 21.2 Hz, +), 108.6 (2C, +), 52.7 (+), 29.7; FTIR (KBr, cm^{-1}): 3163, 3124, 3105, 2952, 1735, 1718, 1701, 1572, 1431, 1389, 1283, 1221, 1115, 1051, 1005, 953, 920, 889, 820, 781, 746, 689, 627; HRMS (TOF ES): Found 249.0097, calculated for $\text{C}_{11}\text{H}_8\text{O}_2\text{FClNa}$ ($\text{M}+\text{Na}$) 249.0095 (0.8 ppm).



methyl 1-(2-bromo-4-fluorophenyl)cycloprop-2-enecarboxylate (19e)

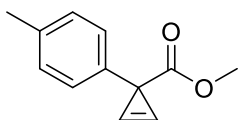
Compound was obtained via typical desilylation procedure using methyl 1-(2-chloro-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate **(18e)** (1.37 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 79% yield (861 mg, 3.18 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.32 (s, 2H), 7.27 (dd, J = 8.3, 2.6 Hz, 1H), 7.16 (dd, J = 8.5, 5.9 Hz, 1H), 6.98 (ddd, J = 8.5, 8.1, 2.6 Hz, 1H), 3.67 (s, 3H); ^{13}C (126 MHz, CDCl_3): δ 175.0, 161.5 (d, J = 250.1 Hz), 138.0 (d, J = 3.4 Hz), 131.3 (d, J = 8.6 Hz, +), 125.3 (d, J = 9.6 Hz), 120.0 (d, J = 24.4 Hz, +), 114.9 (d, J = 21.1 Hz, +), 108.8 (2C, +), 52.8 (+), 31.8; FTIR (KBr, cm^{-1}): 3161, 3121, 2951, 1736, 1718, 1655, 1597, 1578, 1483, 1433, 1383, 1283, 1259, 1236, 1003, 910, 878, 866, 820, 781, 746, 671, 627; HRMS (TOF ES): Found 269.9691, calculated for $\text{C}_{11}\text{H}_8\text{O}_2\text{FBr}$ ($\text{M}+$) 269.9692 (0.4 ppm).



methyl 1-(naphthalen-1-yl)cycloprop-2-enecarboxylate (19f)

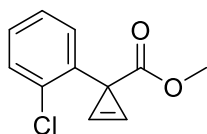
Compound was obtained via typical desilylation procedure using methyl 1-(naphthalen-1-yl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate **(18f)**

(1.19 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a yellow solid in 96% yield (865 mg, 3.86 mmol); mp: 71.4-72.8 °C; ^1H NMR (400 MHz, CDCl_3): 8.09 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.50 (s, 2H), 7.49 – 7.42 (m, 1H), 7.40 – 7.33 (m, 1H), 3.63 (s, 3H); ^{13}C (126 MHz, CDCl_3): 176.5, 138.9, 133.8, 132.2, 128.8 (+), 127.9 (+), 126.2 (+), 125.9 (+), 125.8 (+, 2C), 124.3 (+), 109.3 (+, 2C), 52.6 (+), 29.4; FTIR (KBr, cm^{-1}): 3155, 3113, 3061, 3043, 3003, 2951, 1718, 1657, 1595, 1508, 1433, 1394, 1286, 1252, 1229, 1180, 1080, 1051, 991, 804, 781, 762, 762, 741, 640, 603; HRMS (TOF ES): Found 233.0755, Calculated for $\text{C}_{15}\text{H}_{11}\text{O}_2$ (M-H) 223.0759 (1.8 ppm).



methyl 1-(p-tolyl)cycloprop-2-enecarboxylate (19g)

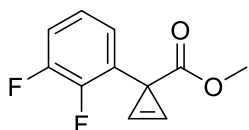
Compound was obtained via typical desilylation procedure using methyl 1-(p-tolyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18g**) (1.04 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 89% yield (673 mg, 3.58 mmol); ^1H NMR (400 MHz, CDCl_3): 7.23 (s, 2H), 7.18 (d, J = 8.2, 2H), 7.13 (d, J = 8.4 Hz, 2H) 3.71 (s, 3H), 2.34 (s, 3H); ^{13}C (126 MHz, CDCl_3): 175.8, 138.6, 136.3, 129.0 (2C, +), 128.2 (2C, +), 107.9 (2C, +), 52.4 (+), 30.4, 21.2 (+); FTIR (KBr, cm^{-1}): 3155, 3111, 3047, 3022, 2995, 2951, 2922, 2843, 2359, 2332, 1907, 1720, 1659, 1514, 1433, 1288, 1225, 1209, 1184, 1113, 1034, 1005, 814, 770, 743, 625; HRMS (TOF ES): Found 211.0741, Calculated for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Na}$ (M+Na) 211.0735 (2.8 ppm).



methyl 1-(2-chlorophenyl)cycloprop-2-enecarboxylate (19i)

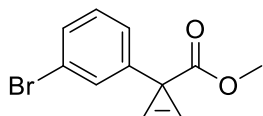
Compound was obtained via typical desilylation procedure using methyl 1-(2-chlorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18i**) (1.04 g,

4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 67% yield (557 mg, 2.67 mmol); ^1H NMR (400 MHz, CDCl_3): 7.37 – 7.33 (m, 1H), 7.33 (s, 2H), 7.25 – 7.16 (m, 3H), 3.67 (s, 3H); ^{13}C (126 MHz, CDCl_3): 175.3, 140.1, 135.1, 130.1 (+), 129.4 (+), 128.5 (+), 127.1 (+), 108.6 (2C, +), 52.6 (+), 30.3; FTIR (KBr, cm^{-1}): 3157, 3117, 3059, 3018, 2951, 2359, 2341, 1718, 1655, 1474, 1433, 1290, 1248, 1221, 1130, 1115, 1061, 1038, 1022, 1005, 901, 878, 793, 758, 746, 733, 706, 650, 608; HRMS (TOF ES): Found 215.0450, Calculated for $\text{C}_{11}\text{H}_9\text{ClO}_2\text{Li}$ (M+Li) 215.0451 (0.5 ppm).



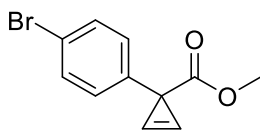
methyl 1-(2,3-difluorophenyl)cycloprop-2-enecarboxylate (19j)

Compound was obtained via typical desilylation procedure using methyl 1-(2,3-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18j**) (1.12 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 mg, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 81% yield (677 mg, 3.22 mmol); ^1H NMR (400 MHz, CDCl_3): 7.28 (s, 2H), 7.09 – 6.96 (m, 2H), 6.92 – 6.86 (m, 1H), 3.68 (s, 3H); ^{13}C (126 MHz, CDCl_3): 174.8, 150.6 (dd, $J = 248.0, 12.9$ Hz), 149.8 (dd, $J = 247.8, 12.6$ Hz), 131.7 (d, $J = 12.5$ Hz), 124.8 (t, $J = 3.1$ Hz, +), 124.0 (dd, $J = 7.0, 4.6$ Hz, +), 116.2 (d, $J = 17.3$ Hz, +), 107.7 (d, $J = 1.5$ Hz, 2C, +), 52.7 (+), 27.0 – 25.2 (m); FTIR (KBr, cm^{-1}): 3165, 3121, 3038, 3001, 2955, 2361, 1720, 1663, 1624, 1591, 1477, 1437, 1304, 1265, 1240, 1217, 1167, 1132, 1053, 976, 881, 866, 854, 816, 791, 762, 746, 721, 631; HRMS (TOF ES): Found 210.0491, Calculated for $\text{C}_{11}\text{H}_8\text{F}_2\text{O}_2$ (M+) 210.0492 (0.5 ppm)



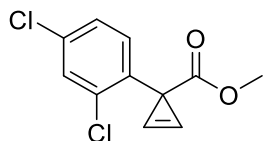
methyl 1-(3-bromophenyl)cycloprop-2-enecarboxylate (19k)

Compound was obtained via typical desilylation procedure using methyl methyl 1-(3-bromophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18k**) (510 mg, 1.57 mmol, 1.0 equiv.) dissolved in THF (2.55 mL) and potassium carbonate (866 mg, 6.27 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 86% yield (344 mg, 1.36 mmol); ^1H NMR (400 MHz, CDCl_3): 7.42 – 7.39 (m, 1H), 7.37 – 7.33 (m, 1H), 7.24 – 7.20 (m, 1H), 7.19 (s, 2H), 7.19 – 7.13 (m, 1H), 3.70 (s, 3H); ^{13}C (126 MHz, CDCl_3): 174.9, 143.9, 131.5 (+), 129.8 (+), 129.8 (+), 127.1 (+), 122.3, 107.4 (2C, +), 52.5 (+), 30.3; FTIR (KBr, cm^{-1}): 3157, 3117, 3061, 2997, 2951, 2361, 1718, 1661, 1593, 1560, 1475, 1433, 1414, 1283, 1265, 1221, 1111, 1072, 1032, 1011, 997, 916, 883, 783, 743, 710, 689, 650, 604; HRMS (TOF ES): Found 274.9686, Calculated for $\text{C}_{11}\text{H}_9\text{BrO}_2\text{Na}$ ($\text{M}+\text{Na}$) 274.9684 (0.7 ppm).



methyl 1-(4-bromophenyl)cycloprop-2-enecarboxylate (19l)

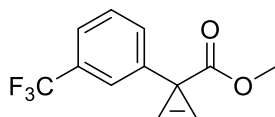
Compound was obtained via typical desilylation procedure using methyl 1-(4-bromophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18l**) (1.30 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 91% yield (917 mg, 3.62 mmol); ^1H NMR (400 MHz, CDCl_3): 7.42 (d, J = 8.5 Hz, 2H), 7.19 (s, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.70 (s, 3H); ^{13}C (126 MHz, CDCl_3): 175.1, 140.6, 131.3 (2C, +), 130.1 (2C, +), 120.6, 107.5 (2C, +), 52.5 (+), 30.2; FTIR (KBr, cm^{-1}): 3157, 3117, 3026, 2997, 2951, 2361, 1718, 1711, 1649, 1483, 1433, 1394, 1288, 1217, 1113, 1070, 1030, 1009, 897, 868, 820, 787, 743, 717, 692, 609; HRMS (TOF ES): Found 274.9684, Calculated for $\text{C}_{11}\text{H}_9\text{BrO}_2\text{Na}$ ($\text{M}+\text{Na}$) 274.9684 (0.0 ppm)



methyl 1-(2,4-dichlorophenyl)cycloprop-2-enecarboxylate (19m)

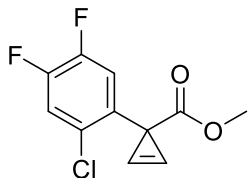
Compound was obtained via typical desilylation procedure using methyl 1-(2,4-dichlorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate

(18m) (1.26 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 71% yield (693 mg, 2.85 mmol); ^1H NMR (400 MHz, CDCl_3): 7.35 (d, $J = 2.2$ Hz, 1H), 7.30 (s, 2H), 7.19 (dd, $J = 8.2, 2.1$ Hz, 1H), 7.12 (d, $J = 8.2$ Hz, 1H), 3.66 (s, 3H); ^{13}C (126 MHz, CDCl_3): 174.8, 138.8, 135.8, 133.5, 131.1 (+), 129.3 (+), 127.4 (+), 108.4 (2C, +), 52.7 (+), 29.7; FTIR (KBr, cm^{-1}): 3161, 3119, 2997, 2951, 2361, 1720, 1663, 1587, 1556, 1474, 1434, 1377, 1296, 1286, 1244, 1229, 1119, 1103, 1061, 1020, 1005, 903, 879, 868, 810, 770, 748, 673, 617; HRMS (TOF ES): Found 264.9804, Calculated for $\text{C}_{11}\text{H}_8\text{Cl}_2\text{O}_2\text{Na}$ ($\text{M}+\text{Na}$) 264.9799 (1.9 ppm)



methyl 1-(3-(trifluoromethyl)phenyl)cycloprop-2-enecarboxylate (19n)

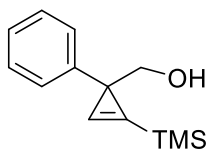
Compound was obtained via typical desilylation procedure using methyl 1-(3-(trifluoromethyl)phenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate **(18n)** (1.26 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 93% yield (902 mg, 3.72 mmol); ^1H NMR (400 MHz, CDCl_3): 7.53 – 7.46 (m, 3H), 7.45 – 7.38 (m, 1H), 7.23 (d, $J = 0.6$ Hz, 2H), 3.71 (d, $J = 0.6$ Hz, 3H); ^{13}C (126 MHz, CDCl_3): 174.9, 142.5, 131.9 (d, $J = 1.3$ Hz, +), 130.6 (q, $J = 32.0$ Hz), 128.6 (+), 125.2 (q, $J = 3.9$ Hz, +), 124.3 (q, $J = 272.3$ Hz), 123.5 (q, $J = 3.8$ Hz, +), 107.4 (2C, +), 52.5 (+), 30.4; FTIR (KBr, cm^{-1}): 3163, 3121, 3003, 2955, 2361, 1718, 1664, 1491, 1439, 1333, 1292, 1277, 1259, 1213, 1163, 1122, 1097, 1072, 1036, 1014, 918, 903, 802, 764, 743, 702, 687, 644, 604; HRMS (TOF ES): Found 249.0714, Calculated for $\text{C}_{12}\text{H}_9\text{F}_3\text{O}_2\text{Li}$ ($\text{M}+\text{Li}$) 249.0715 (0.4 ppm).



**methyl 1-(2-chloro-4,5-difluorophenyl)cycloprop-2-enecarboxylate
(19o)**

Compound was obtained via typical desilylation procedure using methyl 1-(2-chloro-4,5-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18o**) (1.27 g, 4.0 mmol, 1.0 equiv.) dissolved in THF (6.50 mL) and potassium carbonate (2.21 g, 16.0 mmol, 4.0 equiv.). The titled compound was obtained as a pale yellow oil in 69% yield (678 mg, 2.77 mmol); ^1H NMR (400 MHz, CDCl_3): 7.29 (s, 2H), 7.19 (dd, $J = 9.9, 7.2$ Hz, 1H), 7.0 (dd, $J = 10.3, 8.2$ Hz, 1H), 3.67 (s, 3H); ^{13}C (126 MHz, CDCl_3): 174.5, 149.4 (dd, $J = 251.4, 13.6$ Hz), 149.2 (dd, $J = 249.3, 12.6$ Hz), 137.1 (t, $J = 4.6$ Hz), 129.8 (dd, $J = 7.9, 3.5$ Hz), 118.7 (d, $J = 18.2$ Hz, +), 118.6 (d, $J = 20.2$ Hz, +), 108.3 (2C, +), 52.8 (+), 29.8; FTIR (KBr, cm^{-1}): 3163, 3121, 3051, 2955, 2361, 1728, 1661, 1603, 1497, 1437, 1398, 1310, 1258, 1225, 1200, 1173, 1113, 1055, 987, 889, 854, 802, 770, 748, 669, 658, 629, 608; HRMS (TOF ES): Found 243.0017, Calculated for $\text{C}_{11}\text{H}_6\text{ClF}_2\text{O}_2$ (M-H) 243.0024 (2.9 ppm).

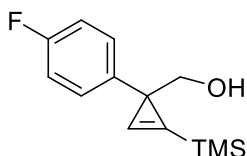
1.10.5 Reduction of TMS-Protected Cyclopropenes



(1-phenyl-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23a)

(Typical Ester Reduction Procedure) An oven dried two neck flask was charged with methyl 1-phenyl-2-(trimethylsilyl)cycloprop-2-enecarboxylate

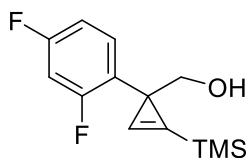
(18a) (1.0 g, 4.06 mmol, 1.0 equiv.) and diethyl ether (10 mL) under a nitrogen atmosphere. The mixture was cooled to -78 °C and DIBAL-H (1.21 g, 1.52 mL, 8.52 mmol, 2.10 equiv.) was then added very slowly dropwise via syringe. Upon complete addition, the reaction was stirred for one hour while maintaining -78 °C. The mixture was then allowed to warm to room temperature, stirred for one hour, and then saturated aqueous ammonium chloride was added dropwise until the solution became a gel. A 10% aqueous solution of HCl solution was then added very slowly until just the moment when the gel dissolves. Ether (10 mL) was added to the solution and the aqueous layer was extracted (3 x 10 mL). Combined organic layers were washed with saturated sodium bicarbonate, brine, dried with magnesium sulfate, filtered, and concentrated. The recovered product was then purified by column chromatography using 6:1 hexane:ethyl acetate mobile phase to provide the titled compound as a white solid in 87% yield (771 mg, 3.53 mmol); mp: 37.2 - 37.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.70 (s, 1H), 7.31 – 7.26 (m, 2H), 7.22 – 7.12 (m, 3H), 4.17 (d, *J* = 11.0 Hz, 1H), 3.99 (d, *J* = 11.0 Hz, 1H), 1.36 (s, 1H), 0.18 (s, 9H); ¹³C (126 MHz, CDCl₃): δ 146.9, 128.1 (2C, +), 126.1 (2C, +), 125.3 (+), 124.0, 123.5 (+), 68.9 (-), 30.1, -0.9 (3C, +); FTIR (KBr, cm⁻¹): 3389, 3057, 3022, 2957, 2897, 2870, 1693, 1599, 1495, 1445, 1408, 1250, 1065, 1013, 989, 866, 843, 756, 727, 698; HRMS (TOF ES): Found 217.1050, calculated for C₁₃H₁₇OSi (M-H) 217.1049 (0.5 ppm).



(1-(4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-

yl)methanol (23b)

Compound was obtained via typical ester reduction procedure using methyl 1-(4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18b**) (397 mg, 1.5 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a pale yellow solid in 75% yield (267 mg, 1.13 mmol); mp: 40.8 – 41.4 °C ^1H NMR (400 MHz, CDCl_3): δ 7.70 (s, 1H), 7.13 (dd, J = 8.9, 5.3 Hz, 2H), 6.95 (t, J = 8.8 Hz, 2H), 4.13 (d, J = 11.5 Hz, 1H), 3.94 (d, J = 11.6 Hz, 1H), 1.35 (s, 1H), 0.16 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 161.0 (d, J = 243.2 Hz), 142.6 (d, J = 3.1 Hz), 127.6 (d, J = 7.7 Hz, 2C, +), 124.6, 123.6 (+), 114.8 (d, J = 21.3 Hz, 2C, +), 69.2 (-), 29.6, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3396, 3377, 3367, 2959, 2899, 2872, 2361, 1691, 1603, 1508, 1410, 1250, 1229, 1159, 1059, 1013, 989, 868, 843, 814, 760, 727, 717; HRMS (TOF ES): Found 243.1200, calculated for $\text{C}_{13}\text{H}_{17}\text{FOSiLi}$ ($\text{M}+\text{Li}$) 243.1193 (2.9 ppm).

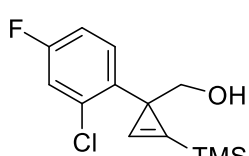


(1-(2,4-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-

yl)methanol (23c)

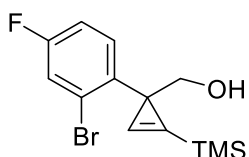
Compound was obtained via typical ester reduction procedure using methyl 1-(2,4-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18c**) (424 mg, 1.50 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a white solid in 80% yield (305 mg, 1.20 mmol); mp: 57.7 – 58.8 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.02 (s, 1H), 7.07 (td, J = 8.4, 6.4 Hz, 1H), 6.81 – 6.69 (m, 2H), 3.96 (d, J = 11.0 Hz, 1H), 3.67 (d, J = 11.2 Hz, 1H), 1.24 (s, 1H), 0.19 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 161.8 (dd, J = 247.2, 11.8 Hz), 161.5 (dd, J = 246.7, 12.0 Hz), 131.1 (dd, J = 9.5, 7.0 Hz, +), 129.0 (dd, J = 16.3, 3.7 Hz), 129.0, 127.0 (+), 111.2 (dd, J = 20.8, 3.6 Hz, +), 103.9 (dd, J =

27.0, 25.1 Hz, +), 69.8 (d, $J = 3.1$ Hz, -), 27.5, -1.3 (3C, +); FTIR (KBr, cm^{-1}): 3259, 3244, 2957, 2872, 1693, 1609, 1601, 1502, 1464, 1418, 1269, 1250, 1136, 1099, 1053, 1022, 966, 881, 843, 818, 760, 741, 731, 717, 700, 615; HRMS (TOF ES): Found 254.0943, calculated for $\text{C}_{13}\text{H}_{16}\text{F}_2\text{OSi}$ (M^+) 254.0938 (2.0 ppm).



(1-(2-chloro-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23d)

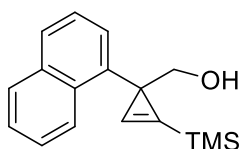
Compound was obtained via typical ester reduction procedure using methyl 1-(2-chloro-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18d**) (448 mg, 1.5 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μL , 3.15 mmol, 2.1 equiv.). The titled compound was obtained as a white solid in 53% yield (214 mg, 0.790 mmol); mp: 61.7 – 63.2 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 8.13 (s, 1H), 7.20 (dd, $J = 8.5, 6.2$ Hz, 1H), 7.06 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.90 (td, $J = 8.3, 2.6$ Hz, 1H), 3.90 (d, $J = 11.2$ Hz, 1H), 3.71 (d, $J = 11.2$ Hz, 1H), 1.09 (s, 1H), 0.24 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 161.3 (d, $J = 248.0$ Hz), 139.6 (d, $J = 3.6$ Hz), 135.0 (d, $J = 10.3$ Hz), 132.2 (d, $J = 8.7$ Hz, +), 129.4, 129.1 (+), 117.0 (d, $J = 24.5$ Hz, +), 114.3 (d, $J = 20.7$ Hz, +), 69.1 (-), 31.3, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3398, 3379, 3360, 3342, 2959, 2899, 2870, 1680, 1599, 1580, 1485, 1408, 1389, 1250, 1223, 1192, 1068, 1036, 1014, 995, 939, 876, 843, 820, 760, 741, 717; HRMS (TOF ES): Found 270.0643, calculated for $\text{C}_{13}\text{H}_{16}\text{ClFOSi}$ (M^+) 270.0643 (0.0 ppm).



(1-(2-bromo-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23e)

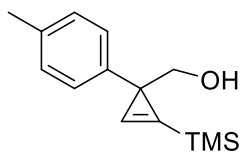
Compound was obtained via typical ester reduction procedure using methyl 1-(2-bromo-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18e**) (515

mg, 1.50 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a pale yellow solid in 62% yield (292 mg, 0.926 mmol); mp: 51.6 – 52.8 $^{\circ}$ C; ^1H NMR (400 MHz, CDCl_3): δ 8.15 (s, 1H), 7.26 – 7.19 (m, 2H), 6.95 (td, J = 8.3, 2.6 Hz, 1H), 3.85 (d, J = 11.2 Hz, 1H), 3.74 (d, J = 11.2 Hz, 1H), 1.13 (s, 1H), 0.26 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 161.1 (d, J = 249.1 Hz), 141.2 (d, J = 3.6 Hz), 132.5 (d, J = 8.4 Hz, +), 129.7 (+), 129.3, 124.4 (d, J = 9.5 Hz), 120.1 (d, J = 24.1 Hz, +), 114.8 (d, J = 20.7 Hz, +), 68.9 (-), 33.2, -0.9 (3C, +); FTIR (KBr, cm^{-1}): 3394, 3381, 3366, 2959, 2899, 2868, 1682, 1595, 1580, 1479, 1410, 1383, 1250, 1221, 1196, 1065, 1032, 1014, 993, 889, 860, 843, 820, 760, 739, 717; HRMS (TOF ES): Found 321.0299, calculated for $\text{C}_{13}\text{H}_{16}\text{BrFOSiLi}$ ($\text{M}+\text{Li}$) 321.0298 (0.3 ppm).



(1-(naphthalen-1-yl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23f)

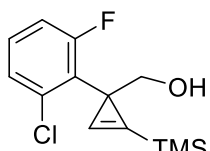
Compound was obtained via typical ester reduction procedure using methyl 1-(naphthalen-1-yl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18f**) (445 mg, 1.50 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.1 equiv.). The titled compound was obtained as a light brown oil in 53% yield (213 mg, 0.794 mmol); ^1H NMR (400 MHz, CDCl_3): δ 8.38 – 8.35 (m, 2H), 7.88 – 7.85 (m, 1H), 7.76 – 7.71 (m, 1H), 7.59 – 7.41 (m, 3H), 7.40 (s, 1H), 3.96 (d, J = 11.6 Hz, 1H), 3.89 (d, J = 11.1 Hz, 1H), 1.39 (s, 1H), 0.28 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 142.5, 134.2, 131.9, 130.9 (+), 129.9, 128.9 (+), 127.3 (+), 126.6 (+), 125.9 (+), 125.8 (+), 125.7 (+), 125.0 (+), 69.9 (-), 31.3, -0.8 (3C, +); FTIR (KBr, cm^{-1}): 3441, 3423, 3406, 3389, 3344, 3059, 3045, 2955, 2899, 2864, 2361, 1732, 1680, 1593, 1508, 1393, 1250, 1020, 887, 843, 800, 779; HRMS (TOF ES): Found 291.1183, calculated for $\text{C}_{17}\text{H}_{20}\text{OSiNa}$ ($\text{M}+\text{Na}$) 291.1181 (0.7 ppm).



(1-(p-tolyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23g)

Compound was obtained via typical ester reduction procedure using methyl 1-(p-tolyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18g**)

(391 mg, 1.50 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.1 equiv.). The titled compound was obtained as a pale yellow solid in 83% yield (288 mg, 1.24 mmol); mp: 53.2-54.0 $^{\circ}$ C; 1 H NMR (400 MHz, CDCl_3): δ 7.70 (s, 1H), 7.13 – 7.04 (m, 4H), 4.13 (dd, J = 11.0, 5.1 Hz, 1H), 3.97 (dd, J = 11.4, 5.1 Hz, 1H), 2.31 (s, 3H), 1.15 (s, 1H), 0.18 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 143.8, 134.8, 128.9 (2C, +), 126.1 (2C, +), 124.2, 124.0 (+), 68.9 (-), 29.9, 21.0 (+), -0.9 (3C, +); FTIR (KBr, cm^{-1}): 3398, 3385, 3022, 2993, 2957, 2920, 2899, 2868, 2361, 1690, 1512, 1466, 1408, 1250, 1061, 1018, 993, 868, 843, 760, 725. HRMS (TOF ES): Found 232.1283, calculated for $\text{C}_{14}\text{H}_{20}\text{OSi}$ (M^+) 232.1283 (0.0 ppm).

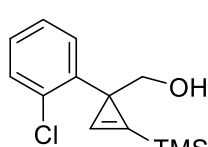


(1-(2-chloro-6-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23h)

Compound was obtained via typical ester reduction procedure using methyl

1-(2-chloro-6-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18h**) (448 mg, 1.50 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.1 equiv.). The titled compound was obtained as a white solid in 64% yield (259 mg, 0.957 mmol); mp: 64.1 – 65.0 $^{\circ}$ C; 1 H NMR (400 MHz, CDCl_3): δ 8.13 (s, 1H), 7.20 (dd, J = 8.5, 6.2 Hz, 1H), 7.06 (dd, J = 8.6, 2.6 Hz, 1H), 6.90 (td, J = 8.3, 2.6 Hz, 1H), 3.90 (d, J = 11.2 Hz, 1H), 3.71 (d, J = 11.2 Hz, 1H), 1.08 (s, 1H), 0.24 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 161.3 (d, J = 248.0 Hz), 139.6 (d, J = 3.6 Hz), 135.0 (d, J = 10.3 Hz), 132.2 (d, J = 8.8 Hz, +), 129.4, 129.2 (+), 117.0 (d, J = 24.4 Hz, +), 114.3 (d, J = 20.8 Hz, +), 69.1 (-), 31.3, -1.0 (2C, +); FTIR (KBr, cm^{-1}): 3369, 3360, 2959, 1682, 1601, 1580, 1485, 1250,

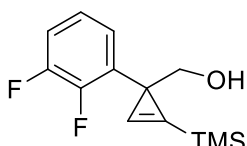
1225, 1068, 1034, 1014, 993, 937, 876, 843, 820, 760, 741, 717; HRMS (TOF ES): Found 271.0724, calculated for $C_{13}H_{17}ClFOSi$ (M+H) 271.0721 (1.1 ppm).



(1-(2-chlorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol

(23i)

Compound was obtained via typical ester reduction procedure using methyl 1-(2-chlorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate **(18i)** (421 mg, 1.5 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a pale yellow solid in 63% yield (240 mg, 0.947 mmol); mp: 61.8 – 63.3 $^{\circ}$ C; 1H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.22 (m, 1H), 7.20 – 7.11 (m, 2H), 3.94 (d, J = 11.2 Hz, 1H), 3.74 (d, J = 11.1 Hz, 1H), 1.09 (s, 1H), 0.24 (s, 9H); ^{13}C (126 MHz, $CDCl_3$): δ 143.5, 134.4, 131.3 (+), 129.9 (+), 129.4 (+), 129.4, 128.0 (+), 127.1 (+), 69.1 (-), 32.0, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3389, 2957, 2899, 2870, 1682, 1468, 1431, 1250, 1074, 1038, 1014, 993, 885, 841, 744, 735, 719; HRMS (TOF ES): Found 259.0898, calculated for $C_{13}H_{17}ClOSiLi$ (M+Li) 259.0897 (0.4 ppm).

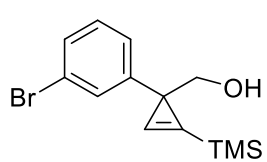


(1-(2,3-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-

yl)methanol (23j)

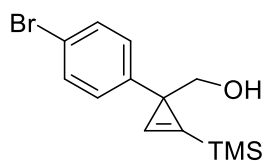
Compound was obtained via typical ester reduction procedure using methyl 1-(2,3-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate **(18j)** (424 mg, 1.50 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a white solid in 77% yield (292 mg, 1.15 mmol); mp: 64.3-64.8 $^{\circ}$ C; 1H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.02 – 6.92 (m, 2H), 6.89 – 6.83 (m, 1H), 4.00 (dd, J = 11.2, 5.8 Hz, 1H), 3.72 (dd, J = 11.2, 5.4 Hz, 1H), 1.19 (t, J = 6.0 Hz, 1H), 0.20 (s,

9H); ^{13}C (126 MHz, CDCl_3): δ 150.8 (dd, $J = 247.8, 13.7$ Hz), 149.9 (dd, $J = 246.0, 12.5$ Hz), 135.7 (d, $J = 12.4$ Hz), 128.5, 126.6 (+), 125.0 (t, $J = 3.6$ Hz, +), 124.0 (dd, $J = 7.1, 4.4$ Hz, +), 115.1 (d, $J = 17.3$ Hz, +), 69.7 (d, $J = 3.1$ Hz, -), 27.9 (d, $J = 2.7$ Hz), -1.3 (3C, +); FTIR (KBr, cm^{-1}): 3240, 3124, 2959, 2876, 1697, 1620, 1585, 1474, 1456, 1435, 1250, 1211, 1063, 1032, 903, 864, 841, 814, 787, 760, 733; HRMS (TOF ES): Found 253.0859, calculated for $\text{C}_{13}\text{H}_{15}\text{F}_2\text{OSi}$ (M-H) 253.0860 (0.4 ppm).



(1-(3-bromophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23k)

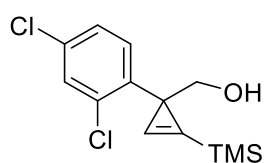
Compound was obtained via typical ester reduction procedure using methyl 1-(3-bromophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18k**) (488 mg, 1.50 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μL , 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a white solid in 90% yield (400 mg, 1.35 mmol); mp: 58.5 – 59.7 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.65 (s, 1H), 7.30 (d, $J = 1.1$ Hz, 1H), 7.28 – 7.23 (m, 1H), 7.13 (d, $J = 5.0$ Hz, 2H), 4.12 (d, $J = 10.8$ Hz, 1H), 3.93 (d, $J = 11.1$ Hz, 1H), 1.26 (s, 1H), 0.18 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 149.8, 129.6 (+), 129.3 (+), 128.2 (+), 124.8 (+), 123.7, 122.7 (+), 122.6, 68.9 (-), 29.8, -0.9 (3C, +); FTIR (KBr, cm^{-1}): 3296, 3283, 3119, 2959, 2935, 2897, 2878, 1693, 1591, 1562, 1472, 1462, 1416, 1410, 1250, 1076, 1055, 1015, 995, 872, 843, 787, 758, 725, 702; HRMS (TOF ES): Found 295.0146, calculated for $\text{C}_{13}\text{H}_{16}\text{BrOSi}$ (M-H) 295.0154 (2.7 ppm).



(1-(4-bromophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23l)

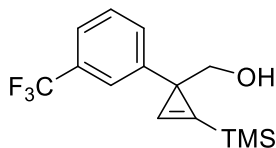
Compound was obtained via typical ester reduction procedure using methyl 1-(4-bromophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18l**) (488 mg, 1.50

mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a white solid in 95% yield (423 mg, 1.14 mmol); mp: 58.5 – 58.9 $^{\circ}$ C; ^1H NMR (400 MHz, CDCl_3): δ 7.65 (s, 1H), 7.37 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 4.12 (d, J = 11.1 Hz, 1H), 3.92 (d, J = 11.1 Hz, 1H), 1.26 (s, 1H), 0.16 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 146.2, 131.0 (2C, +), 127.9 (2C, +), 123.9, 122.8 (+), 119.0, 69.0 (-), 29.7, -0.9 (3C, +); FTIR (KBr, cm^{-1}): 3371, 3356, 2957, 2897, 2872, 1693, 1487, 1406, 1394, 1250, 1076, 1055, 1007, 989, 868, 843, 762, 737, 717; HRMS (TOF ES): Found 295.0151, calculated for $\text{C}_{13}\text{H}_{16}\text{BrOSi}$ (M-H) 295.0154 (1.0 ppm).



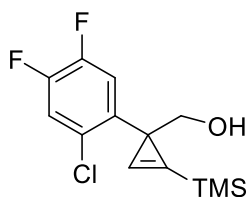
(1-(2,4-dichlorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23m)

Compound was obtained via typical ester reduction procedure using methyl 1-(2,4-dichlorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18m**) (473 mg, 1.50 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a pale yellow solid in 74% yield (319 mg, 1.11 mmol); mp: 60.3 – 61.4 $^{\circ}$ C; ^1H NMR (400 MHz, CDCl_3): δ 8.11 (s, 1H), 7.35 – 7.30 (m, 1H), 7.16 – 7.15 (m, 2H), 3.91 (d, J = 11.2 Hz, 1H), 3.70 (d, J = 11.2 Hz, 1H), 1.13 (s, 1H), 0.24 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 142.2, 135.1, 132.8, 132.2 (+), 129.6 (+), 129.3, 128.8 (+), 127.4 (+), 69.0 (-), 31.4, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3363, 2957, 2899, 2870, 1682, 1585, 1553, 1470, 1410, 1375, 1250, 1101, 1074, 1036, 1014, 993, 932, 887, 843, 822, 800, 760, 741, 719, 702; HRMS (TOF ES): Found 285.0274, calculated for $\text{C}_{13}\text{H}_{15}\text{Cl}_2\text{OSi}$ (M-H) 285.0269 (1.8 ppm).



(1-(3-(trifluoromethyl)phenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23n)

Compound was obtained via typical ester reduction procedure using methyl 1-(3-(trifluoromethyl)phenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18n**) (472 mg, 1.50 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a white solid in 81% yield (349 mg, 1.22 mmol); mp: 53.8 – 54.3 $^{\circ}$ C; ^1H NMR (400 MHz, CDCl_3): δ 7.67 (s, 1H), 7.59 – 7.33 (m, 4H), 4.17 (d, J = 11.2 Hz, 1H), 3.99 (d, J = 11.2 Hz, 1H), 1.25 (s, 1H), 0.18 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 148.3, 130.4 (q, J = 31.8 Hz), 129.5 (d, J = 1.4 Hz, +), 128.5 (+), 124.5 (q, J = 272.3 Hz) 123.6, 122.9 (q, J = 3.8 Hz, +), 122.7 (+), 121.9 (q, J = 3.8 Hz, +), 69.1 (-), 29.9, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3360, 2961, 2901, 2874, 1697, 1612, 1591, 1435, 1331, 1252, 1163, 1124, 1097, 1078, 1063, 1014, 868, 843, 800, 702; HRMS (TOF ES): Found 285.0924, calculated for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{OSi}$ (M-H) 285.0923 (0.4 ppm).

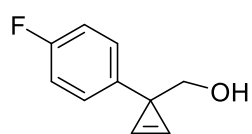


(1-(2-chloro-4,5-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (23o)

Compound was obtained via typical ester reduction procedure using methyl 1-(2-chloro-4,5-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**18o**) (475 mg, 1.5 mmol, 1.0 equiv.), diethyl ether (4.0 mL), and DIBAL-H (448 mg, 562 μ L, 3.15 mmol, 2.10 equiv.). The titled compound was obtained as a pale yellow solid in 57% yield (245 mg, 0.848 mmol); mp: 98.4 – 99.8 $^{\circ}$ C; ^1H NMR (400 MHz, CDCl_3): δ 8.08 (s, 1H), 7.15 (dd, J = 10.0, 7.3 Hz, 1H), 7.03 (dd, J = 10.7, 8.4 Hz, 1H), 3.90 (d, J = 11.2 Hz, 1H), 3.70 (d, J = 11.2 Hz, 1H), 1.10 (s, 1H), 0.24 (s, 9H); ^{13}C (126 MHz, CDCl_3): δ 149.2 (dd, J = 249.2, 12.4 Hz), 148.9 (dd, J = 250.3, 13.7 Hz), 140.7, 129.3, 128.8 (dd, J = 7.9, 3.3 Hz), 128.5 (+), 119.4 (d, J = 17.6 Hz, +), 118.7 (d, J = 20.0 Hz,

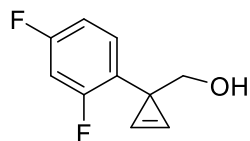
+, 69.0 (-), 31.5, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3240, 2962, 2880, 1688, 1599, 1497, 1462, 1387, 1302, 1275, 1252, 1171, 1080, 1020, 878, 841, 798, 760, 739, 719, 700, 679, 633; HRMS (TOF ES): Found 289.0627, calculated for $\text{C}_{13}\text{H}_{16}\text{ClF}_2\text{OSi}$ ($\text{M}+\text{H}$) 289.0627 (0.0 ppm).

1.10.6 Reduction of Deprotected Cyclopropenes



(1-(4-fluorophenyl)cycloprop-2-en-1-yl)methanol (20b)

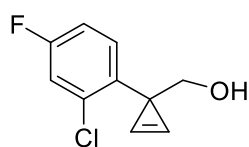
Compound was obtained via typical ester reduction procedure using methyl 1-(4-fluorophenyl)cycloprop-2-enecarboxylate (**19b**) (182 mg, 0.947 mmol, 1.0 equiv.), diethyl ether (2.5 mL), and DIBAL-H (283 mg, 355 μL , 1.99 mmol, 2.10 equiv.). The titled compound was obtained as a pale yellow oil in 79% yield (123 mg, 0.748 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.35 (s, 2H), 7.22 – 7.15 (m, 2H), 7.02 – 6.94 (m, 2H), 4.04 (s, 2H), 1.45 (s, 1H); ^{13}C (126 MHz, CDCl_3): δ 161.4 (d, $J = 244.2$ Hz), 141.5 (d, $J = 3.1$ Hz), 128.0 (d, $J = 7.8$ Hz, 2C, +), 115.0 (d, $J = 21.0$ Hz, 2C, +), 113.5 (2C, +), 68.3 (-), 28.8; FTIR (KBr, cm^{-1}): 3423, 3404, 3387, 3364, 3346, 2926, 2876, 1641, 1601, 1502, 1474, 1406, 1225, 1159, 1099, 1067, 1011, 997, 968, 839, 818, 669, 611; HRMS (TOF ES): Found 171.0798, calculated for $\text{C}_{10}\text{H}_9\text{OFLi}$ ($\text{M}+\text{Li}$) 171.0797 (0.6 ppm).



(1-(2,4-difluorophenyl)cycloprop-2-en-1-yl)methanol (20c)

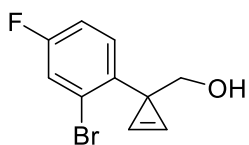
Compound was obtained via typical ester reduction procedure using methyl 1-(2,4-difluorophenyl)cycloprop-2-enecarboxylate (**19c**) (139 mg, 0.660 mmol, 1.0 equiv.), diethyl ether (1.75 mL), and DIBAL-H (197 mg, 247 μL , 1.39 mmol, 2.10 equiv.). The titled compound was obtained as a pale yellow solid in 79% yield (94.5 mg, 0.519 mmol); mp: 59.5 – 61.2 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.57 (s, 2H), 7.17 – 7.09 (m, 1H), 6.83 – 6.70 (m, 2H), 3.84 (s, 2H), 1.32 (s, 1H); ^{13}C (126 MHz, CDCl_3): δ 161.8 (d, $J = 247.4$ Hz),

161.7 (d, $J = 247.5$ Hz), 131.0 (dd, $J = 9.6, 6.8$ Hz, +), 128.2 (dd, $J = 16.2, 3.8$ Hz), 116.2 (d, $J = 1.7$ Hz, 2C, +), 111.3 (dd, $J = 21.0, 3.7$ Hz, +), 104.1 (dd, $J = 26.6, 25.0$ Hz, +), 68.7 (d, $J = 2.5$ Hz, -), 26.4; FTIR (KBr, cm^{-1}): 3259, 3246, 3142, 3105, 2935, 2878, 1637, 1609, 1595, 1501, 1462, 1425, 1294, 1267, 1138, 1103, 1051, 1024, 1001, 984, 964, 851, 812, 729, 669, 623, 611; HRMS (TOF ES): Found 181.0468, calculated for $\text{C}_{10}\text{H}_7\text{OF}_2$ (M-H) 181.0465 (1.7 ppm).



(1-(2-chloro-4-fluorophenyl)cycloprop-2-en-1-yl)methanol (20d)

Compound was obtained via typical ester reduction procedure using methyl 1-(2-chloro-4-fluorophenyl)cycloprop-2-enecarboxylate (**19d**) (113 mg, 0.496 mmol, 1.0 equiv.), diethyl ether (1.5 mL), and DIBAL-H (148 mg, 186 μL , 1.04 mmol, 2.10 equiv.). The titled compound was obtained as a pale yellow oil in 91% yield (89.4 mg, 0.450 mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.62 (s, 2H), 7.23 (dd, $J = 8.5, 6.2$ Hz, 1H), 7.06 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.91 (td, $J = 8.3, 2.6$ Hz, 1H), 3.80 (s, 2H), 1.36 (s, 1H); ^{13}C (126 MHz, CDCl_3): δ 161.4 (d, $J = 248.4$ Hz), 138.8 (d, $J = 3.6$ Hz), 134.9 (d, $J = 10.4$ Hz), 131.8 (d, $J = 8.7$ Hz, +), 117.0 (d, $J = 24.5$ Hz, +), 116.9 (2C, +), 114.4 (d, $J = 20.7$ Hz, +), 68.0 (-), 29.7; FTIR (KBr, cm^{-1}): 3358, 3111, 2926, 2870, 2361, 1637, 1597, 1578, 1483, 1389, 1258, 1223, 1217, 1198, 1180, 1070, 1043, 1011, 968, 928, 891, 858, 818, 687, 669, 611; HRMS (TOF ES): Found 205.0417, calculated for $\text{C}_{10}\text{H}_8\text{OFClLi}$ (M+Li) 205.0408 (4.4 ppm).

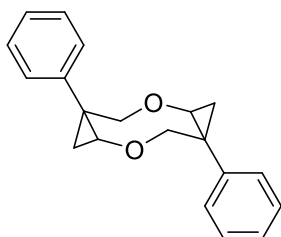


(1-(2-bromo-4-fluorophenyl)cycloprop-2-en-1-yl)methanol (20e)

Compound was obtained via typical ester reduction procedure using methyl 1-(2-bromo-4-fluorophenyl)cycloprop-2-enecarboxylate (**19e**) (128 mg, 0.472 mmol, 1.0 equiv.), diethyl ether (1.5 mL), and DIBAL-H (141 mg, 177 μL , 0.992 mmol, 2.10 equiv.). The titled compound was obtained as a clear oil in 74% yield (85.0 mg, 0.350

mmol); ^1H NMR (400 MHz, CDCl_3): δ 7.63 (s, 2H), 7.27 – 7.21 (m, 2H), 6.96 (td, J = 8.3, 2.6 Hz, 1H), 3.81 (s, 2H), 1.40 (s, 1H); ^{13}C (126 MHz, CDCl_3): δ 161.3 (d, J = 249.4 Hz), 140.4 (d, J = 3.5 Hz), 132.1 (d, J = 8.3 Hz, +), 124.1 (d, J = 9.6 Hz), 120.1 (d, J = 24.4 Hz, +), 117.0 (2C, +), 115.0 (d, J = 20.8 Hz, +), 67.7 (-), 31.5; FTIR (KBr, cm^{-1}): 3321, 2934, 2862, 1637, 1597, 1572, 1477, 1383, 1290, 1256, 1209, 1192, 1178, 1067, 1034, 1011, 968, 922, 858, 818, 729, 708, 663, 608; HRMS (TOF ES): Found 264.9641, calculated for $\text{C}_{10}\text{H}_8\text{OBrNa}$ ($\text{M}+\text{Na}$) 264.9640 (0.4 ppm).

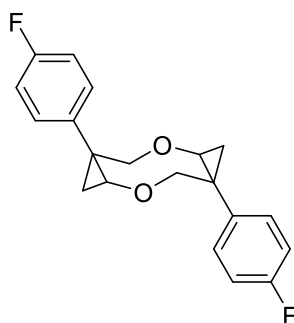
1.10.7 (4+4) Cyclodimerization of Deprotected Cyclopropenes



(1*R,4*R**,6*S**,9*S**)-4,9-diphenyl-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21a)**

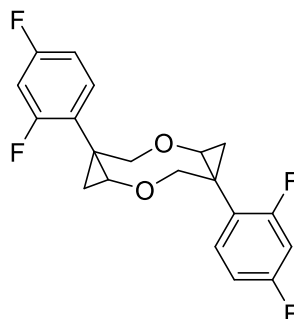
(Typical Cyclization Procedure) (1-phenylcycloprop-2-en-1-yl)methanol (**20a**) (73.1 mg, 0.50 mmol, 1.0 equiv.), 18-C-6 (30.0 mg, 0.113 mmol, 0.225 equiv.), potassium hydroxide (70.2 mg, 1.25 mmol, 2.50 equiv.) and THF (6.0 mL) were placed in an oven dried Wheaton vial (5 mL) equipped with spin vane and mininert valve and stirred overnight at 55 °C. The reaction was then dried with magnesium sulfate, filtered, and concentrated. The product was then purified by column chromatography using a 9:1 hexane:ethyl acetate mobile phase to provide the titled compound as a white solid in 66% yield (19.3 mg, 0.066 mmol.); dr: >98:2; GC (Rt, min): 11.47 (main), 11.34 (minor); mp: 186.6 – 187.4 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.27 (m, 8H), 7.25 – 7.19 (m, 2H), 4.71 (d, J = 12.1 Hz, 2H), 3.73 (dd, J = 6.6, 3.6 Hz, 2H), 3.67 (d, J = 12.1 Hz, 2H), 1.31 – 1.22 (m, 4H); ^{13}C (126 MHz, CDCl_3): δ 142.7 (2C), 128.5 (4C, +), 127.4 (4C, +), 126.4 (2C, +), 76.9 (2C, -), 66.3 (2C, +), 33.3 (2C), 21.7 (2C, -); FTIR (KBr, cm^{-1}): 3084, 3055, 3022, 2986, 2959, 2934, 2876, 1601, 1495, 1454, 1360,

1310, 1269, 1258, 1165, 1070, 1049, 1024, 976, 916, 835, 820, 741, 692; HRMS (TOF ES): Found 292.1465, calculated for $C_{20}H_{20}O_2$ (M^+) 292.1463 (0.7 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-bis(4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21b)**

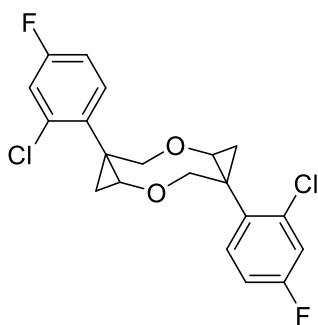
Compound was obtained via typical cyclization procedure using (1-(4-fluorophenyl)cycloprop-2-en-1-yl)methanol (**20b**) (82.2 mg, 0.50 mmol, 1.0 equiv.), 18-C-6 (30.0 mg, 0.113 mmol, 0.225 equiv.), potassium hydroxide (70.2 mg, 1.25 mmol, 2.50 equiv.) and THF (6.0 mL). The titled compound was obtained as a white solid in 63% yield (20.7 mg, 0.063 mmol.); dr: 98:2; GC (*R*_t, min): 11.30; mp: 209.1 – 210.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.28 – 7.23 (m, 4H), 7.03 – 6.95 (m, 4H), 4.62 (d, *J* = 12.0 Hz, 2H), 3.66 (dd, *J* = 8.01, 3.91 Hz, 2H), 3.63 (d, *J* = 12.0 Hz, 2H), 1.30 – 1.18 (m, 4H); ¹³C (126 MHz, CDCl₃): δ 161.6 (d, *J* = 244.8 Hz, 2C), 138.3 (d, *J* = 3.1 Hz, 2C), 129.3 (d, *J* = 7.8 Hz, 4C, +), 115.3 (d, *J* = 21.3 Hz, 4C, +), 77.2 (2C, -), 66.0 (2C, +), 33.0 (2C), 21.4 (2C, -); FTIR (KBr, cm⁻¹): 2947, 2912, 2889, 2862, 2357, 2339, 2330, 1595, 1512, 1504, 1487, 1454, 1232, 1217, 1161, 1074, 1036, 926, 841, 812, 729; HRMS (TOF ES): Found 327.12, calculated for $C_{20}H_{17}F_2O_2$ ($M-H$) 327.1197 (0.9 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-bis(2,4-difluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21c)**

Compound was obtained via typical cyclization procedure using (1-(2,4-difluorophenyl)cycloprop-2-en-1-yl)methanol (**20c**) (91.0 mg, 0.50 mmol, 1.0 equiv.), 18-C-6 (30.0 mg, 0.113 mmol, 0.225 equiv.), potassium hydroxide (70.2 mg, 1.25 mmol, 2.50 equiv.) and THF (6.0 mL). The titled compound

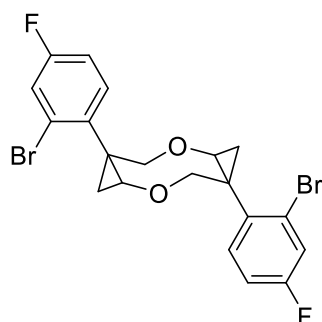
was obtained as a white solid in 59% yield (21.5 mg, 0.059 mmol.); dr: 94-6; GC (Rt, min): 10.71 (main), 10.77 (minor); mp: 205 – 208.2 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.34 – 7.26 (m, 2H), 6.86 – 6.72 (m, 4H), 4.52 (d, *J* = 12.0 Hz, 2H), 3.82 (d, *J* = 12.1 Hz, 2H), 3.78 (dd, *J* = 6.8, 3.5 Hz, 2H), 1.29 (dd, *J* = 6.4, 3.5 Hz, 2H), 1.08 (t, *J* = 6.6 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 162.3 (dd, *J* = 250.6, 12.4 Hz, 2C), 162.1 (dd, *J* = 247.7, 11.7 Hz, 2C), 133.0 (dd, *J* = 9.7, 5.8 Hz, 2C, +), 125.2 (dd, *J* = 13.5, 3.8 Hz, 2C), 111.4 (dd, *J* = 20.9, 3.6 Hz, 2C, +), 104.3 (t, *J* = 25.6 Hz, 2C, +), 77.3 (2C, -), 63.8 (d, *J* = 1.5 Hz, 2C, +), 29.5 (2C), 20.8 (2C, -); FTIR (KBr, cm⁻¹): 3063, 2986, 2953, 2874, 2359, 2339, 1614, 1595, 1504, 1462, 1423, 1362, 1312, 1263, 1231, 1163, 1140, 1097, 1078, 1045, 1034, 966, 851, 812, 741, 731, 615; HRMS (TOF ES): Found 363.01, calculated for C₂₀H₁₅F₄O₂ (M-H) 363.1008 (2.2 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-bis(2-chloro-4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21d)**

Compound was obtained via typical cyclization procedure using (1-(2-chloro-4-fluorophenyl)cycloprop-2-en-1-yl)methanol (**20d**) (99.3 mg, 0.50 mmol, 1.0 equiv.), 18-C-6 (30.0 mg, 0.113 mmol, 0.225 equiv.), potassium hydroxide (70.2 mg, 1.25 mmol, 2.50 equiv.) and THF (6.0 mL). The titled compound was obtained as a white solid in 75% yield (29.8 mg, 0.075 mmol.); dr: 98:2; GC (Rt, min): 13.08; mp: 234.7 – 236.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.38 (dd, *J* = 8.6, 6.1 Hz, 2H), 7.10 (dd, *J* = 8.5, 2.6 Hz, 2H), 6.95 (td, *J* = 8.3, 2.7 Hz, 2H), 4.67 (d, *J* = 12.0 Hz, 2H), 3.78 (dd, *J* = 6.9, 3.4 Hz, 2H), 3.71 (d, *J* = 12.1 Hz, 2H), 1.38 (dd, *J* = 6.8, 3.5 Hz, 2H), 1.09 (t, *J* = 6.8 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 161.7 (d, *J* = 249.3 Hz, 2C), 136.4 (d, *J* = 10.4 Hz, 2C), 134.7 (d, *J* = 3.6 Hz, 2C), 133.7 (d, *J* = 8.7 Hz, 2C, +), 117.4 (d, *J* = 24.7 Hz, 2C, +), 114.1 (d, *J* = 21.0 Hz, 2C, +), 76.8 (2C, -), 64.9 (2C, +), 33.2 (2C), 22.0 (2C, -); FTIR (KBr, cm⁻¹): 3074, 2976, 2957, 2934, 2874, 2359, 2341, 2330,

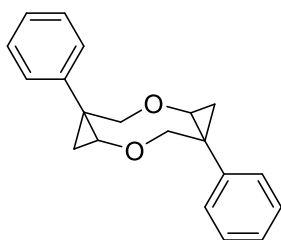
1601, 1574, 1487, 1458, 1392, 1354, 1304, 1258, 1202, 1161, 1080, 1057, 1028, 982, 897, 856, 843, 822, 733; HRMS (TOF ES): 403.0657, calculated for C₂₀H₁₆Cl₂F₂O₂Li (M+Li) 403.0655 (0.5 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-bis(2-bromo-4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21e)**

Compound was obtained via typical cyclization procedure using (1-(2-bromo-4-fluorophenyl)cycloprop-2-en-1-yl)methanol **(20e)** (121.5 mg, 0.50 mmol, 1.0 equiv.), 18-C-6 (30.0 mg, 0.113 mmol, 0.225 equiv.), potassium hydroxide (70.2 mg, 1.25 mmol, 2.50 equiv.) and THF (6.0 mL). The titled compound was obtained as a white solid in 63% yield (30.5 mg, 0.063 mmol.); dr: >98:2; mp: 221 – 223 °C (decomposed); ¹H NMR (400 MHz, CDCl₃): δ 7.38 (dd, *J* = 8.6, 6.0 Hz, 2H), 7.30 (dd, *J* = 8.2, 2.6 Hz, 2H), 7.00 (td, *J* = 8.3, 2.7 Hz, 2H), 4.71 (d, *J* = 12.0 Hz, 2H), 3.77 (dd, *J* = 6.9, 3.4 Hz, 2H), 3.67 (d, *J* = 12.1 Hz, 2H), 1.41 (dd, *J* = 6.8, 3.5 Hz, 2H), 1.11 (t, *J* = 6.9 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 161.6 (d, *J* = 250.3 Hz, 2C), 136.0 (d, *J* = 3.5 Hz, 2C), 133.9 (d, *J* = 8.6 Hz, 2C, +), 125.9 (d, *J* = 9.6 Hz, 2C), 120.6 (d, *J* = 24.3 Hz, 2C, +), 114.6 (d, *J* = 20.9 Hz, 2C, +), 76.8 (2C, -), 65.3 (2C, +), 35.0 (2C), 22.7 (2C, -); FTIR (KBr, cm⁻¹): 3094, 3067, 2972, 2957, 2928, 2889, 2868, 2361, 2345, 1597, 1582, 1487, 1458, 1356, 1306, 1259, 1204, 1163, 1078, 1053, 1024, 978, 881, 841, 816, 804, 731; HRMS (TOF ES): Found 482.9407, calculated for C₂₀H₁₅Br₂F₂O₂ (M-H) 482.9407 (0.0 ppm).

1.10.8 One-Pot Desilylative (4+4) Cyclodimerization of Cyclopropenes



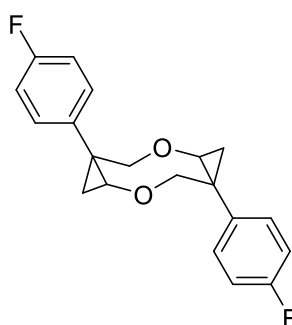
(1*R,4*R**,6*S**,9*S**)-4,9-diphenyl-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane**

(21a)

(Typical One-Pot Desilylative Cyclization Procedure)(1-phenyl-2-

(trimethylsilyl)cycloprop-2-en-1-yl)methanol **(23a)** (29.2 mg, 0.20

mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL) were placed in an oven dried Wheaton vial (5 mL) equipped with spin vane and mininert valve and stirred overnight at 65 °C. The reaction was then dried with magnesium sulfate, filtered, and concentrated. The product was then purified by column chromatography using a 9:1 hexane:ethyl acetate mobile phase to provide the titled compound as a white solid in 64% yield (18.8 mg, 0.064 mmol.); dr: 98:2; Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **20a**.

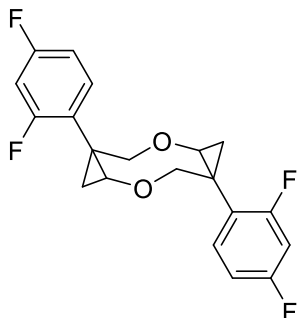


(1*R,4*R**,6*S**,9*S**)-4,9-bis(4-fluorophenyl)-2,7-**

dioxatricyclo[7.1.0.0^{4,6}]decane (21b)

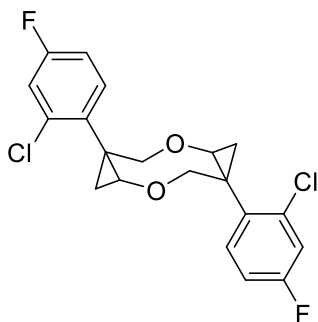
Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol **(23b)** (47.3 mg, 0.2 mmol, 1.0 equiv.), 18-C-6 (12.0

mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.5 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 59% yield (19.3 mg, 0.059 mmol.); dr: 98:2; Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **20b**.



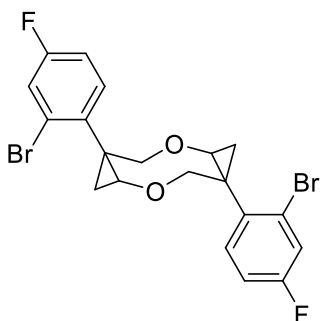
(1*R,4*R**,6*S**,9*S**)-4,9-bis(2,4-difluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21c)**

Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(2,4-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**23c**) (50.9 mg, 0.2 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 62% yield (22.5 mg, 0.062 mmol.); dr:79-21; Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **20c**.



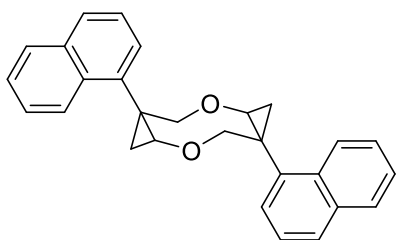
(1*R,4*R**,6*S**,9*S**)-4,9-bis(2-chloro-4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21d)**

Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(2-chloro-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**23d**) (54.2 mg, 0.2 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 79% yield (31.4 mg, 0.079 mmol.); dr: >98:2; Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **20d**.



(1*R,4*R**,6*S**,9*S**)-4,9-bis(2-bromo-4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21e)**

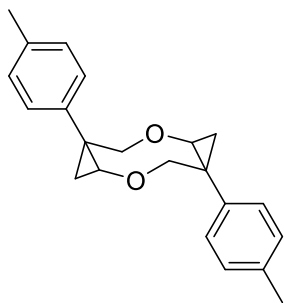
Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(2-bromo-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol **(23e)** (63.1 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 63% yield (30.4 mg, 0.063 mmol.); dr: >98:2; Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **20e**.



(1*R,4*R**,6*S**,9*S**)-4,9-di(naphthalen-1-yl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21f)**

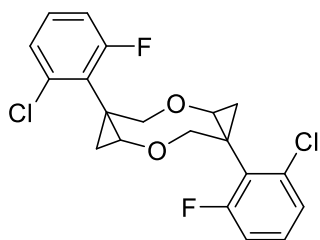
Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(naphthalen-1-yl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol **(23f)** (52.9 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.5 equiv.) and THF (2.2 mL). The titled compound was obtained as a white solid in 55% yield (21.4 mg, 0.055 mmol.); dr: >98:2; mp: 253 – 256 °C (decomposed); ¹H NMR (400 MHz, CDCl₃): δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 5.8 Hz, 2H), 7.58 – 7.43 (m, 6H), 4.83 (d, *J* = 11.6 Hz, 2H), 4.04 (d, *J* = 11.7 Hz, 2H), 3.95 (dd, *J* = 6.8, 3.2 Hz, 2H), 1.61 (dd, *J* = 6.1, 3.2 Hz, 2H), 1.18 (t, *J* = 6.5 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 137.4 (2C), 134.4 (2C), 132.0 (2C), 129.2 (2C, +), 128.6 (2C, +), 128.0 (2C, +), 126.0 (2C, +), 125.7 (2C, +), 125.5 (2C, +), 124.0 (2C, +), 77.6 (2C, -), 64.5 (2C, +), 33.1 (2C), 22.0 (2C, -); FTIR (KBr, cm⁻¹): 3994, 3069, 3047, 2947, 2945,

2922, 2866, 1593, 1504, 1454, 1435, 1400, 1265, 1252, 1153, 1128, 1082, 1061, 1040, 1001, 968, 864, 837, 800, 775, 733, 706, 621; HRMS (TOF ES): Found 391.1695, calculated for C₂₈H₂₃O₂ (M-H) 391.1698 (0.8 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-di-p-tolyl-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21g)**

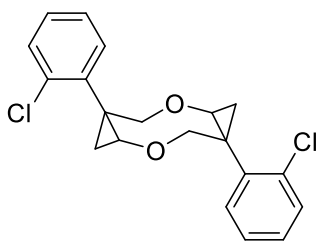
Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(p-tolyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**23g**) (46.5 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.5 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 78% yield (25.0 mg, 0.078 mmol.); dr: >98:2; GC (Rt, min): 12.77; mp: 170.2 – 172.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.18 (d, *J* = 8.2 Hz, 4H), 7.11 (d, *J* = 7.9 Hz, 4H), 4.66 (d, *J* = 12.0 Hz, 2H), 3.68 (dd, *J* = 6.6, 3.6 Hz, 2H), 3.64 (d, *J* = 12.0 Hz, 2H), 2.32 (s, 6H), 1.29 – 1.16 (m, 4H); ¹³C (126 MHz, CDCl₃): δ 139.8 (2C), 136.0 (2C), 129.2 (4C, +), 127.3 (4C, +), 77.0 (2C, -), 66.2 (2C, +), 33.0 (2C), 21.6 (2C, -), 21.1 (2C, +); FTIR (KBr, cm⁻¹): 3088, 3049, 3013, 2982, 2943, 2922, 2872, 2361, 2332, 1518, 1458, 1447, 1360, 1265, 1161, 1113, 1076, 1034, 1020, 978, 835, 787, 739; HRMS (TOF ES): Found 327.1936, calculated for C₂₂H₂₄O₂Li (M+Li) 327.1936 (0.0 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-bis(2-chloro-6-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21h)**

Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(2-chloro-6-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**23h**) (54.2 mg, 0.20 mmol, 1.0 equiv.), 18-C-6

(12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 69% yield (27.3 mg, 0.069 mmol.); dr: >98:2; GC (Rt, min): 13.11; mp: 237 - 240 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.41 – 7.36 (m, 2H), 7.13 – 7.08 (m, 2H), 6.98 – 6.92 (m, 2H), 4.67 (d, *J* = 12.0 Hz, 2H), 3.78 (dd, *J* = 6.8, 3.4 Hz, 2H), 3.71 (d, *J* = 12.6 Hz, 2H), 1.39 (dd, *J* = 6.7, 3.4 Hz, 2H), 1.09 (t, *J* = 6.8 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 161.7 (d, *J* = 249.3 Hz, 2C), 136.4 (d, *J* = 10.3 Hz, 2C), 134.7 (d, *J* = 3.4 Hz, 2C), 133.7 (d, *J* = 8.7 Hz, 2C, +), 117.4 (d, *J* = 24.6 Hz, 2C, +), 114.1 (d, *J* = 21.2 Hz, 2C, +), 76.8 (2C, -), 64.9 (2C, +), 33.2 (2C), 22.0 (2C, -); FTIR (KBr, cm⁻¹): 3074, 2976, 2957, 2935, 2874, 2359, 2332, 1601, 1574, 1487, 1458, 1391, 1354, 1304, 1258, 1202, 1161, 1078, 1057, 1028, 982, 897, 856, 843, 820, 733, 685; HRMS (TOF ES): Found 395.0414, calculated for C₂₀H₁₅Cl₂F₂O₂ (M-H) 395.0417 (0.8 ppm).

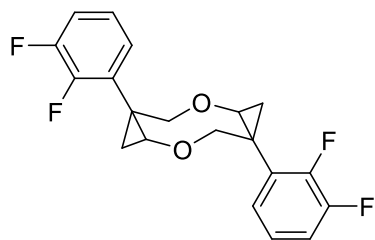


(1*R,4*R**,6*S**,9*S**)-4,9-bis(2-chlorophenyl)-2,7-**

dioxatricyclo[7.1.0.0^{4,6}]decane (21i)

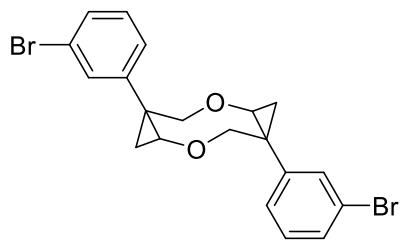
Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(2-chlorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol **(23i)** (50.6 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 62% yield (22.4 mg, 0.062 mmol.); dr: >98:2; GC (Rt, min): 13.11; mp: 233 - 236 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.43 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.35 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.25 – 7.15 (m, 4H), 4.73 (d, *J* = 12.0 Hz, 2H), 3.82 (dd, *J* = 6.8, 3.4 Hz, 2H), 3.77 (d, *J* = 12.0 Hz, 2H), 1.40 (dd, *J* = 6.7, 3.5 Hz, 2H), 1.11 (t, *J* = 6.8 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 138.7 (2C), 135.7 (2C), 132.8 (2C, +), 130.1 (2C, +), 128.5 (2C, +), 126.9 (2C, +), 76.8 (2C, -), 64.9 (2C, +), 33.9 (2C), 22.0 (2C, -); FTIR (KBr, cm⁻¹): 3070, 3055, 2976, 2949, 2932, 2885, 2870, 2359, 1474,

1458, 1433, 1356, 1306, 1288, 1267, 1252, 1188, 1171, 1128, 1080, 1030, 976, 914, 839, 754, 727, 685; HRMS (TOF ES): Found 359.0602, calculated for C₂₀H₁₇Cl₂O₂ (M-H) 359.0606 (1.1 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-bis(2,3-difluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21j)**

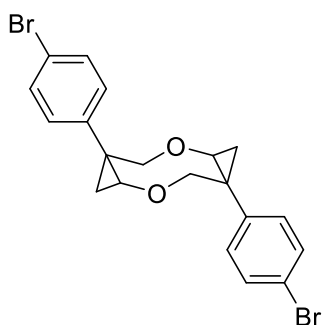
Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(2,3-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol **(23j)** (50.9 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 57% yield (20.9 mg, 0.057 mmol.); dr: 84:16; GC (Rt, min): 11.22 (main), 11.14 (minor); mp: 211 – 214.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.14 – 6.96 (m, 6H), 4.56 (d, *J* = 12.1 Hz, 2H), 3.88 (d, *J* = 12.1 Hz, 2H), 3.84 (dd, *J* = 6.8, 3.5 Hz, 2H), 1.34 (dd, *J* = 6.5, 3.5 Hz, 2H), 1.13 (t, *J* = 6.7 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 150.9 (dd, *J* = 248.2, 13.2 Hz, 2C), 150.5 (dd, *J* = 249.1, 12.5 Hz, 2C), 131.6 (d, *J* = 10.0 Hz, 2C), 126.8 (2C, +), 124.1 (dd, *J* = 7.1, 4.7 Hz, 2C, +), 116.1 (d, *J* = 17.2 Hz, 2C, +), 77.1 (2C, -), 63.6 (2C, +), 29.9 (d, *J* = 2.5 Hz, 2C), 20.9 (d, *J* = 2.2 Hz, 2C, -); FTIR (KBr, cm⁻¹): 3088, 3045, 2976, 2928, 2868, 2363, 1626, 1589, 1474, 1456, 1356, 1312, 1261, 1221, 1190, 1159, 1086, 1065, 1041, 987, 941, 928, 895, 837, 798, 783, 725, 690; HRMS (TOF ES): Found 365.1161, calculated for C₂₀H₁₇F₄O₂ (M+H) 365.1165 (1.1 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-bis(3-bromophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21k)**

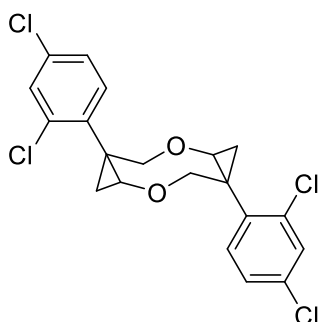
Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(3-bromophenyl)-2-

(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**23k**) (59.5 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 83% yield (37.5 mg, 0.083 mmol.); dr: >98:2; mp: 226 - 230 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.39 (t, *J* = 1.8 Hz, 2H), 7.34 (dt, *J* = 7.6, 1.4 Hz, 2H), 7.23 – 7.14 (m, 4H), 4.66 (d, *J* = 12.1 Hz, 2H), 3.68 (dd, *J* = 6.4, 4.0 Hz, 2H), 3.60 (d, *J* = 12.2 Hz, 2H), 1.33 – 1.23 (m, 4H); ¹³C (126 MHz, CDCl₃): δ 145.0 (2C), 130.5 (2C, +), 130.1 (2C, +), 129.6 (2C, +), 126.1 (2C, +), 122.7 (2C), 76.6 (2C, -), 66.2 (2C, +), 33.2 (2C), 21.9 (2C, -); FTIR (KBr, cm⁻¹): 3078, 3063, 2959, 2956, 2359, 2341, 2332, 1724, 1591, 1560, 1477, 1458, 1433, 1410, 1354, 1254, 1163, 1067, 1032, 835, 797, 771, 744, 735, 696, 669, 621; HRMS (TOF ES): Found 454.9825, calculated for C₂₀H₁₈Br₂O₂Li (M+Li) 454.9834 (2.0 ppm).



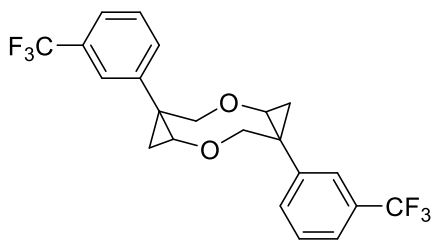
(1*R,4*R**,6*S**,9*S**)-4,9-bis(4-bromophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21l)**

Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(4-bromophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**23l**) (59.5 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 67% yield (30.2 mg, 0.067 mmol.); dr: >98:2; mp: 231.3 - 234 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, *J* = 8.6 Hz, 4H), 7.14 (d, *J* = 8.6 Hz, 4H), 4.64 (d, *J* = 12.1 Hz, 2H), 3.65 (dd, *J* = 6.5, 3.8 Hz, 2H), 3.59 (d, *J* = 12.2 Hz, 2H), 1.30 – 1.19 (m, 4H); ¹³C (126 MHz, CDCl₃): δ 141.6 (2C), 131.6 (4C, +), 129.2 (4C, +), 120.3 (2C), 76.7 (2C, -), 66.2 (2C, +), 32.9 (2C), 21.8 (2C, -); FTIR (KBr, cm⁻¹): 3086, 3059, 2978, 2922, 2864, 1489, 1456, 1394, 1350, 1259, 1163, 1074, 1063, 1043, 1030, 1009, 978, 843, 818, 754, 714; HRMS (TOF ES): Found 454.9839, calculated for C₂₀H₁₈Br₂O₂Li (M+Li) 454.9834 (1.1 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-bis(2,4-dichlorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21m)**

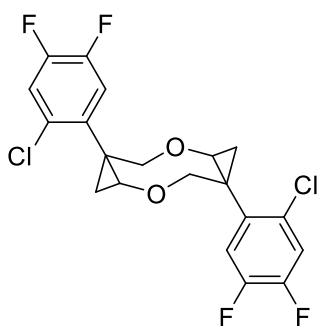
Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(2,4-dichlorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**23m**) (57.5 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid in 65% yield (28.1 mg, 0.065 mmol.); dr: 96:4; mp: 250 – 252 °C (decomposed); ¹H NMR (400 MHz, CDCl₃): δ 7.39 – 7.32 (m, 2H), 7.24 – 7.19 (m, 2H), 4.67 (d, *J* = 12.1 Hz, 2H), 3.77 (dd, *J* = 6.9, 3.5 Hz, 2H), 3.70 (d, *J* = 12.1 Hz, 2H), 1.39 (dd, *J* = 6.8, 3.5 Hz, 2H), 1.09 (t, *J* = 6.9 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 137.3 (2C), 136.4 (2C), 133.8 (2C), 133.5 (2C, +), 129.9 (2C, +), 127.2 (2C, +), 76.6 (2C, -), 64.8 (2C, +), 33.4 (2C), 22.0 (2C, -); FTIR (KBr, cm⁻¹): 3078, 3059, 2972, 2950, 2928, 2872, 1585, 1555, 1474, 1458, 1375, 1356, 1302, 1286, 1263, 1188, 1165, 1103, 1080, 1026, 976, 903, 841, 798, 777, 727, 702; HRMS (TOF ES): Found 426.9818, calculated for C₂₀H₁₅Cl₄O₂ (M-H) 426.9826 (1.9 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-bis(3-(trifluoromethyl)phenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21n)**

Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(3-(trifluoromethyl)phenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**23n**) (57.3 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a white solid

in 70% yield (30.1 mg, 0.070 mmol.); dr: >98:2; GC (Rt, min): 10.83; mp: 137.1 – 140.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.54 – 7.39 (m, 8H), 4.71 (d, *J* = 12.2 Hz, 2H), 3.72 (dd, *J* = 6.6, 3.8 Hz, 2H), 3.66 (d, *J* = 12.2 Hz, 2H), 1.41 – 1.28 (m, 4H); ¹³C (126 MHz, CDCl₃): δ 155.8 (q, *J* = 31.2 Hz, 2C), 143.6 (2C), 131.0 (2C, +), 129.0 (2C, +), 124.3 (q, *J* = 272.4 Hz, 2C), 124.1 (q, *J* = 3.9 Hz, 2C, +), 123.3 (q, *J* = 3.8 Hz, 2C, +), 76.6 (2C, -), 66.3 (2C, +), 33.3 (2C), 21.9 (2C, -); FTIR (KBr, cm⁻¹): 3084, 3045, 2980, 2959, 2924, 2872, 2359, 1612, 1593, 1489, 1462, 1445, 1358, 1335, 1296, 1263, 1163, 1119, 1074, 1049, 1038, 978, 841, 798, 735, 700, 662; HRMS (TOF ES): Found 428.1211, calculated for C₂₂H₁₈F₆O₂ (M⁺) 428.1211 (0.0 ppm).

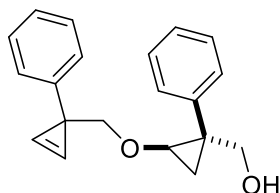


(1*R,4*R**,6*S**,9*S**)-4,9-bis(2-chloro-4,5-difluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (21o)**

Compound was obtained via typical one-pot desilylative cyclization procedure using (1-(2-chloro-4,5-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**23o**) (57.8 mg, 0.20 mmol, 1.0 equiv.), 18-C-6 (12.0 mg, 0.045 mmol, 0.225 equiv.), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv.) and THF (2.20 mL). The titled compound was obtained as a pale yellow solid in 32% yield (13.9 mg, 0.032 mmol.); dr: 98:2; GC (Rt, min): 12.57 (main), 12.64 (minor); mp: 239 – 242 °C (decomposition); ¹H NMR (400MHz, CDCl₃): δ 7.23 – 7.17 (m, 4H), 4.67 (d, *J* = 12.2 Hz, 2H), 3.76 (dd, *J* = 6.9, 3.5 Hz, 2H), 3.65 (d, *J* = 12.2 Hz, 2H), 1.43 (dd, *J* = 6.9, 3.5 Hz, 2H), 1.13 (t, *J* = 6.9 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 149.4 (dd, *J* = 251.9, 13.6 Hz, 2C), 148.8 (dd, *J* = 249.4, 12.6 Hz, 2C), 135.5 – 135.4 (m, 2C), 130.4 (dd, *J* = 7.9, 3.4 Hz, 2C), 121.1 (d, *J* = 17.9 Hz, 2C, +), 119.1 (d, *J* = 20.2 Hz, 2C, +), 76.6 (2C, -), 64.8 (2C, +), 33.5 (2C), 22.2 (2C, -); FTIR (KBr, cm⁻¹): 3065, 3051, 2972, 2959, 2926, 2870, 1736, 1599, 1495, 1460, 1410, 1315, 1267, 1244, 1180,

1148, 1121, 1078, 1059, 1040, 993, 922, 879, 839, 800, 739, 650, 625; HRMS (TOF ES): Found 439.0471, calculated for $C_{20}H_{14}Cl_2F_4O_2Li$ (M+Li) 439.0467 (0.9 ppm).

1.10.9 Isolation of linear dimer



((1*R,2*R**)-1-Phenyl-2-((1-phenylcycloprop-2-en-1-yl)methoxy)-cyclopropyl)methanol (**25a**):**

An oven dried Wheaton vial (5 mL) equipped with spin vane and Mininert valve was charged with (1- phenylcycloprop-2-en-1-yl)methanol (50.0 mg, 0.342 mmol, 1.00 equiv.), 18-crown-6 ether (20.0 mg, 0.076 mmol, 0.225 equiv.), powdered potassium hydroxide (48.0 mg, 0.855 mmol, 2.50 equiv) and THF (4.0 mL). The mixture was stirred for approximately one hour at 45 °C closely monitored by TLC. Retention factors of starting alcohol **20a**, intermediate **25a**, and cyclic product **21a** are 0.19, 0.31, and 0.59, respectively (eluent - hexane:EtOAc 3:1). When maximum concentration of the spot with *R_f* 0.31 (hexane:EtOAc 3:1) was observed, anhydrous magnesium sulfate was immediately added to the reaction mixture, which was then filtered, and concentrated. The intermediate **25a** was isolated by preparative column chromatography eluting with a mixture of hexane and ethyl acetate (3:1) to afford a pale yellow oil in 9% yield (9.0 mg, 0.031 mmol); 1H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.10 (m, 12H), 4.02 (d, *J* = 10.3 Hz, 1H), 3.97 (d, *J* = 10.3 Hz, 1H), 3.94 (d, *J* = 11.6 Hz, 1H), 3.76 (d, *J* = 11.6 Hz, 1H), 3.51 (dd, *J* = 6.5, 3.6 Hz, 1H), 1.73 (s, 1H), 1.09 (dd, *J* = 6.1, 3.6 Hz, 1H), 1.01 (t, *J* = 6.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 129.0, 128.8 (2C, +), 128.6 (2C, +), 128.5, 128.1 (2C, +), 126.7 (+), 126.3 (2C, +), 125.8 (+), 112.9 (2C, +), 78.4 (+), 66.2 (-), 63.4 (-), 33.6, 17.2 (-), 11.4; FTIR (KBr, cm^{-1}): 3445, 3099, 3082, 3057, 3024, 2930, 2868, 1645, 1601, 1495, 1447, 1393, 1360, 1161, 1072,

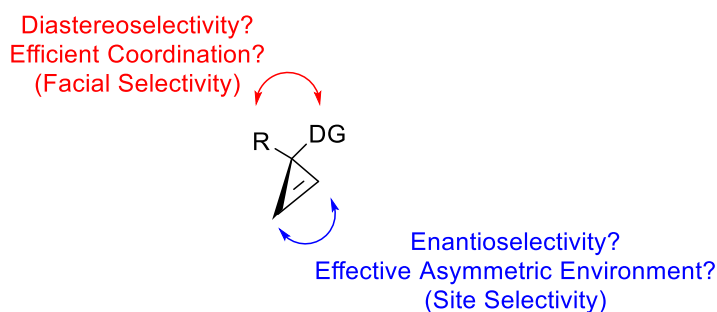
1026, 918, 752, 698, 636, 569, 542; HRMS (TOF ES): Found 291.1384, calculated for C₂₀H₁₉O₂ (M-H) 291.1391 (3.0 ppm).

Chapter 2. Directed Rh(I)-Catalyzed Asymmetric Hydroboration of Cyclopropenes

2.1 Introduction

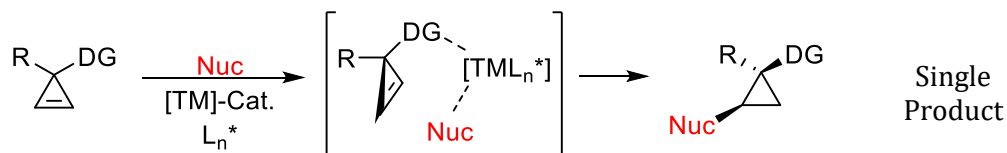
Transition metal-catalyzed additions to cyclopropenes are intriguing transformations due to the ability of ligating the metal with asymmetric ligands, which when perform reactions on 3,3-disubstituted cyclopropenes, provide the possibility of developing simultaneously diastereoselective and enantioselective reactions (**Figure 4**).

Figure 4. Origin of stereoselectivity for reactions involving 3,3-disubstituted cyclopropenes.



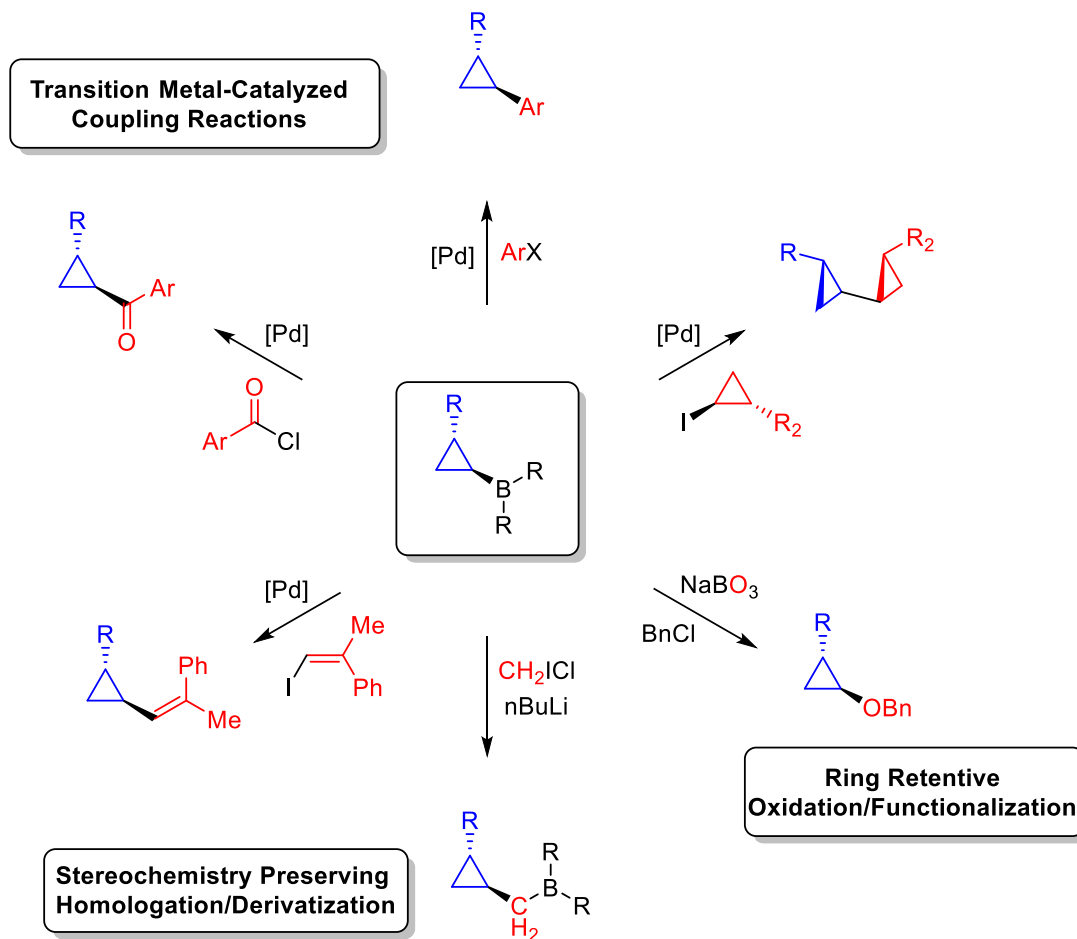
Achieving a high degree of stereoselectivity relies on two independent factors. Diastereoselectivity or facial selectivity is determined by efficient interactions between substituents at C-3 of cyclopropene and the transition-metal catalyst. Enantioselectivity results from efficient site selectivity of the double bond as determined by the asymmetric environment established by chiral ligands attached to the catalyst. Successful incorporation of both forms of selectivity allow for the production of a single stereoisomeric product from prochiral starting materials in a single transformation (**Scheme 13**).

Scheme 13



One motif we have become increasingly interested in are cyclopropylboronates due to their employment during the synthesis of a variety of natural products^[19] and pharmaceuticals,^[20] as well as their utility in synthetic chemistry as surrogates for the cyclopropyl anion (**Scheme 14**).

Scheme 14

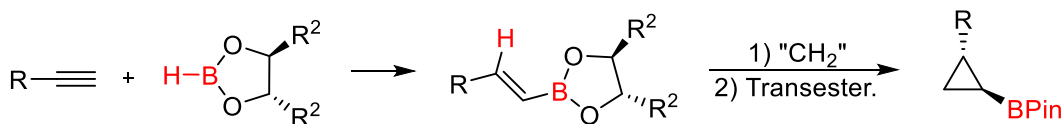


In particular, cyclopropylboronates have been shown to participate in transition metal-catalyzed cross-coupling reactions with a variety of electrophiles including acyl,^[21] aryl,^[22] vinyl,^[23] and cyclopropyl^[24] halides. Additionally, cyclopropylboronates are able to undergo ring retentive oxidation and subsequent functionalization.^[25] Via homologation, the construction of a sp^3 carbon-carbon bond is possible while preserving boron in the molecule and thus allowing further derivatization such as oxidation to alcohols or amines.^[26]

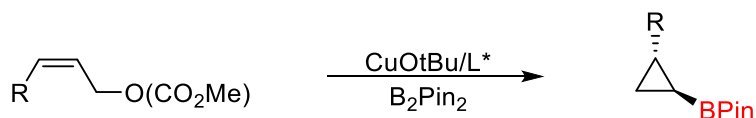
While a few methods for the synthesis of racemic cyclopropylboronates have existed since the mid 1960's,^[27] the synthesis of the optically active variety has only existed since the late 1990's (**Scheme 15**).

Scheme 15

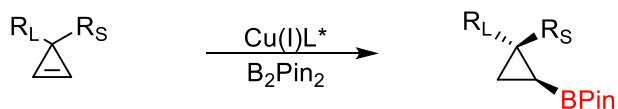
a)



b)



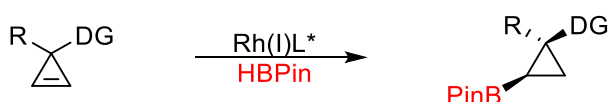
c)



Early methods utilized the placement of a chiral 1,2-diol derived auxiliary on boron. Hydroboration of acetylenes provided borylated olefins, which could then undergo diastereoselective cyclopropanation reactions. Subsequent removal of the chiral auxiliary provided enantioenriched cyclopropylboronates (**Scheme 15a**).^[28] More recently, Ito has reported an asymmetric copper-catalyzed borylation/1,3-cyclization sequence of allylic carbonates (**Scheme 15b**).^[29] However, this reaction was limited to the use of *Z*-configured olefins and was only efficient in the synthesis of *trans*-cyclopropylboronates. In 2014 Lin and Tortosa independently reported copper-catalyzed hydroboration of cyclopropenes in which facial differentiation is controlled by the differing sterics of a small and large substituent in the 3 position of cyclopropene (**Scheme 15c**).^[30]

However, an additional mode of selectivity which delivers boron to the same face of cyclopropane as a large substituent via efficient coordination between a transition metal catalyst and a strategically placed directing group was still desired as this selectivity remained unexplored (**Scheme 16**).

Scheme 16

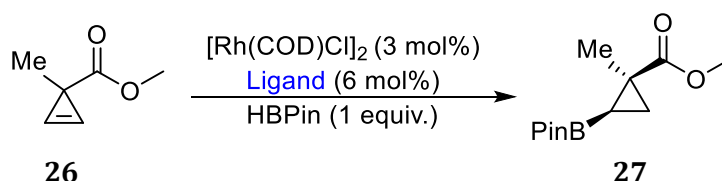


2.2 Initial Reaction Optimization

Initial reaction screening was conducted using cyclopropene **26** with catalyst and ligand systems which had previously been shown to be efficient in the asymmetric hydroboration of olefins.^[31] Early combinations of Rh(I) catalyst with Josiphos, Quinap, and BDPP provided reactivity, however, in rather disappointing efficiencies (**Table 9, entries 1-3**). Due to the

selectivity shown with the BDPP ligand, a survey of other diphosphine ligands was conducted and provided very impressive results. Widely available BINAP provided cyclopropylboronate **27** in nearly quantitative yield along with extremely high diastereo- and enantioselectivity (**Table 9, entry 8**)!^[32]

Table 9. Initial optimization of ester directed CAHB.



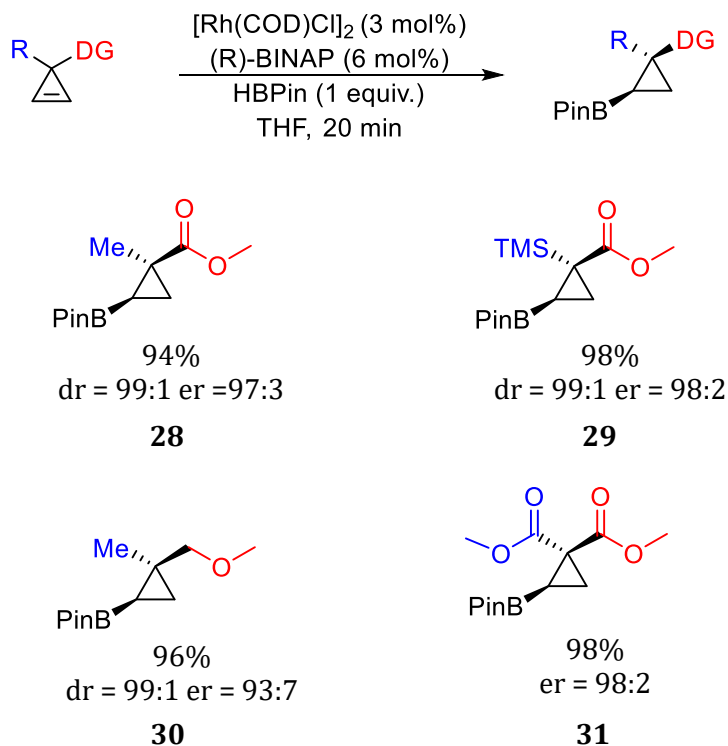
Entry	Ligand	Time, h	Yield, % ^[a]	dr ^[b]	er ^[c]
1	Josiphos (SL-J008-1)	8	47	1:1	82:18
2	(R)-Quinap	8	9	17:83	1:1
3	(S,S)-BDPP	8	43	72:28	83:17
4	(R,R)-Chiraphos	3	47	98:2	94:6
5	(S,S)-Me-Duphos	3	82	99:1	94:6
6	(R)-Phanephos	3	89	99:1	99:1
7	(R,R)-Norphos	1	86	98:2	99:1
8	(R)-BINAP	0.3	96	99:1	99:1

[a] NMR yield measured from crude reaction with dibromomethane as standard.

[b] Determined by GC analysis of crude reaction. [c] Determined by GC analysis using CYCLODEX B chiral column.

With this result in hand, a variety of different cyclopropenes were surveyed to evaluate the generality of the developed protocol (**Table 10**). The reaction proved to be highly efficient both with ester **28** and ether **30** as a directing group. Furthermore, the placement of a sterically encumbered TMS group and a relatively small methyl group on the opposing face of cyclopropenes **29** and **28** provided high degree of diastereo- and enantioselectivity.^[32]

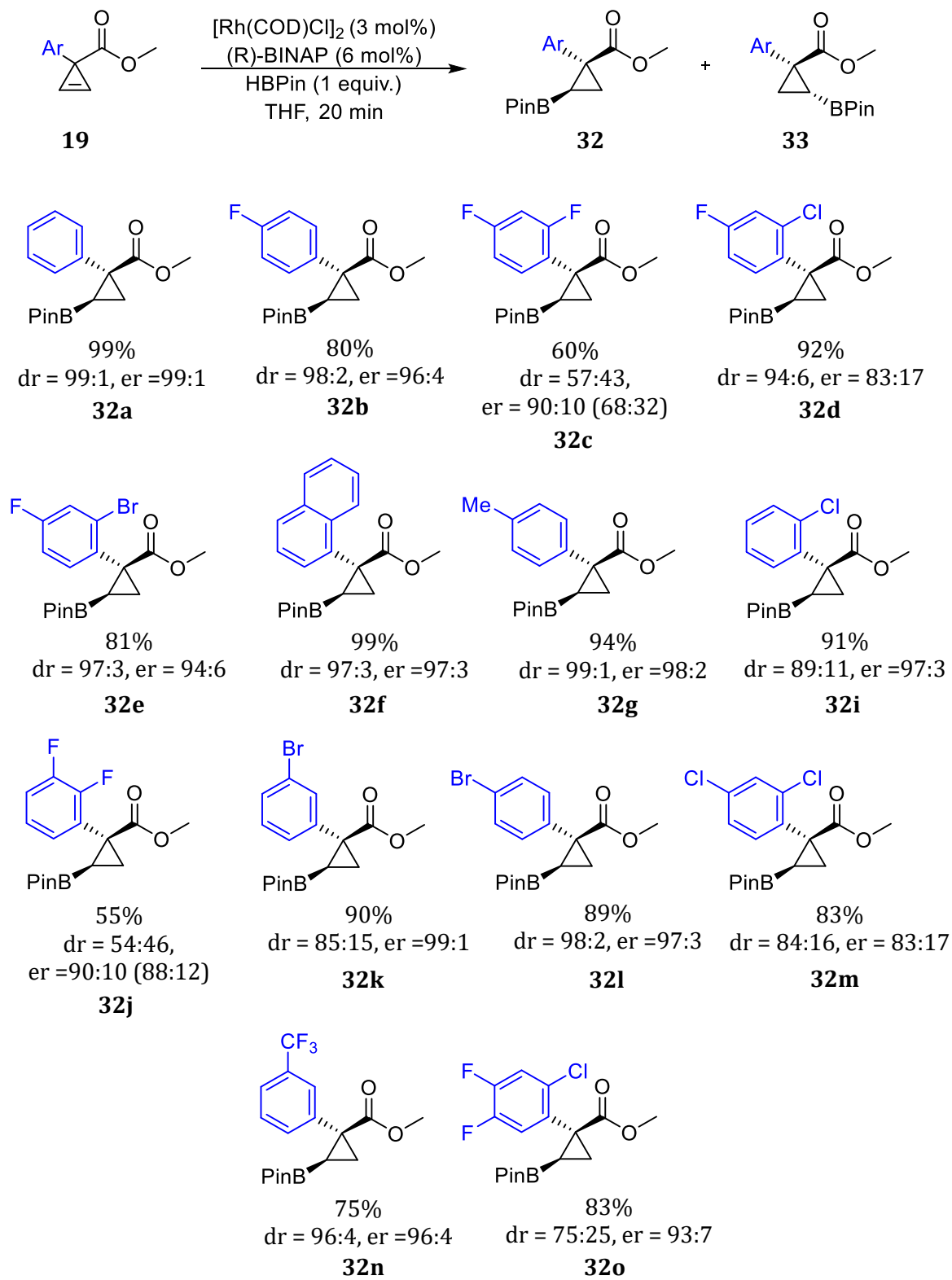
Table 10. Evaluation of optimized CAHB conditions on various cyclopropene substrates.



2.3 Directed Catalytic Asymmetric Hydroboration of Cyclopropenylcarboxylates

The newly developed expedited synthesis of 3,3-disubstituted cyclopropenes via Rh(II)-catalyzed cyclopropanation of TMS-acetylene followed by desilylation, as discussed in chapter I, allowed for a thorough evaluation of the directed catalytic asymmetric hydroboration reaction across a wide variety of prochiral substrates **19** possessing an ester as directing group (**Table 11**). The reaction was found to be extremely efficient with relatively neutral phenyl-, naphthyl-, and tolyl-substituted examples **32a**, **32f**, and **32g** respectively.

Table 11. Directed CAHB of cyclopropenylcarboxylates.



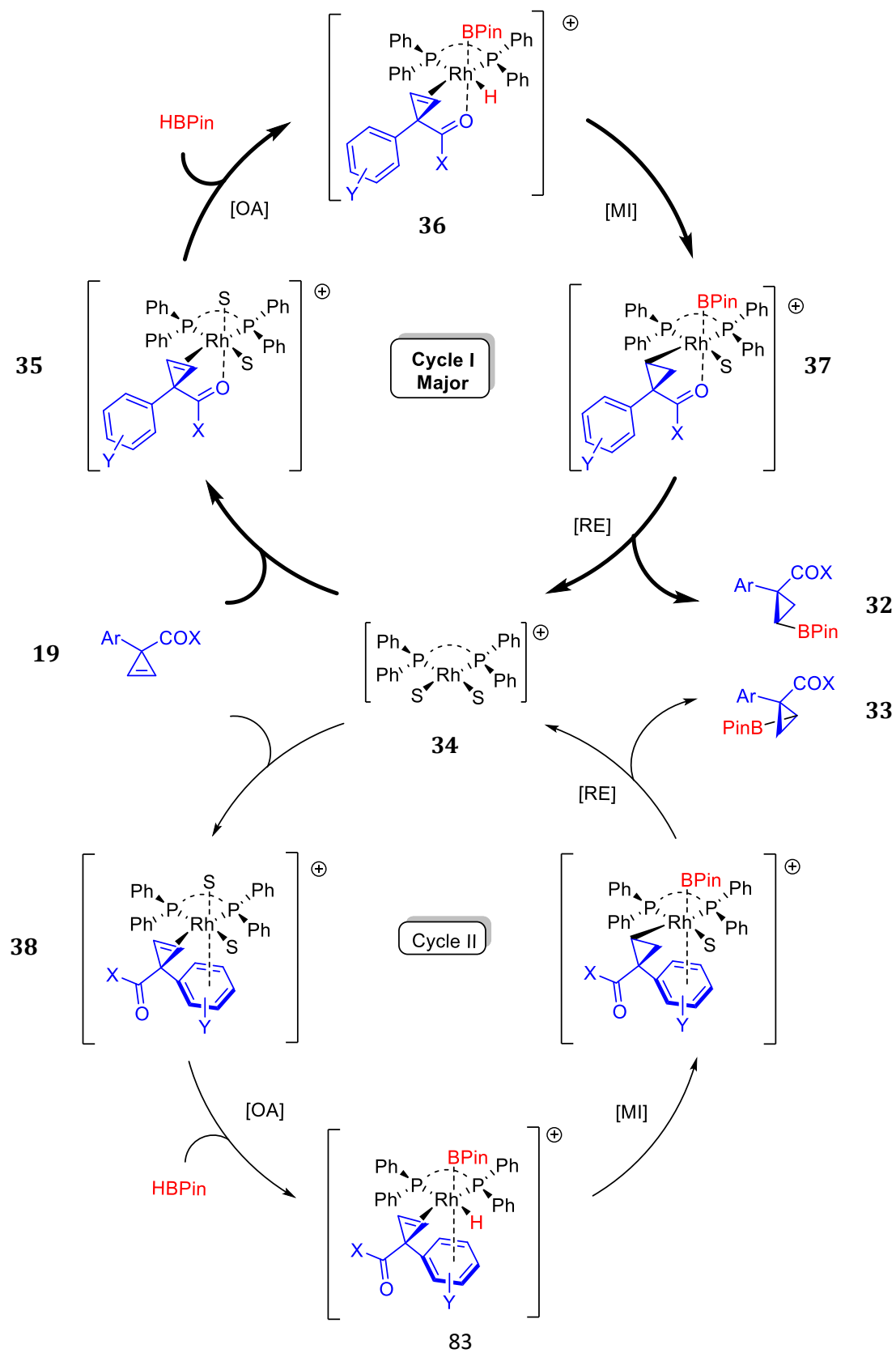
Additionally, placement of electron-withdrawing halogens at the 3 or 4 position of the aryl ring provided high yield, diastereo-, and enantioselectivity. Surprisingly, placement of a halogen in the 2 position resulted in a reduced yield and diastereoselectivity. Specifically, the placement of fluorine in the 2 position drastically reduced yield and almost completely eroded diastereoselectivity, as seen in examples **32c** and **32j**.

2.4 Discussion of Proposed Mechanism

With the obtained results, a possible operating mechanism is proposed^[33], to rationalize the outcomes observed in **Table 11 (Scheme 17)**. The process would begin with chiral rhodium(I) species **34** coordinating to prochiral cyclopropene **19**. This coordination could occur through the carbonyl to produce **35** (cycle I). Subsequent oxidative addition of rhodium into the H-B bond of pinacolborane could then provide Rh(III) intermediate **36**. Diastereo- and enantiodefining hydorrhodation of the cyclopropene double bond would result in chiral cyclopropyl rhodium(III) complex **37**. Reductive elimination to form the C-B bond would return the catalytically active species **34** and produce cyclopropylboronate **32** with a *cis*-configuration of the directing group and boron.

Alternatively, cycle II may explain the poor diastereoselectivity observed in several examples presented in **Table 11**. The competitive formation of species **38** could occur during substrate coordination, possibly due to the proper geometrical orientation between the electron-deficient transition metal and electron-rich fluorine. It is also possible this interaction^[34] plays a significant role in stabilizing complexes formed from substrates possessing fluorine substituents in the 2-position of the aryl ring. Proceeding through cycle II results in oxidative addition into the B-H bond, hydorrhodation of cyclopropene, and reductive elimination to produce cyclopropylboronate **33** with a *trans*-configuration of the directing group and boron.

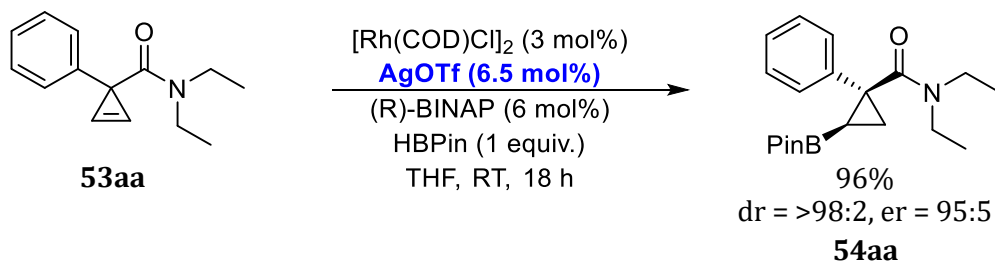
Scheme 17



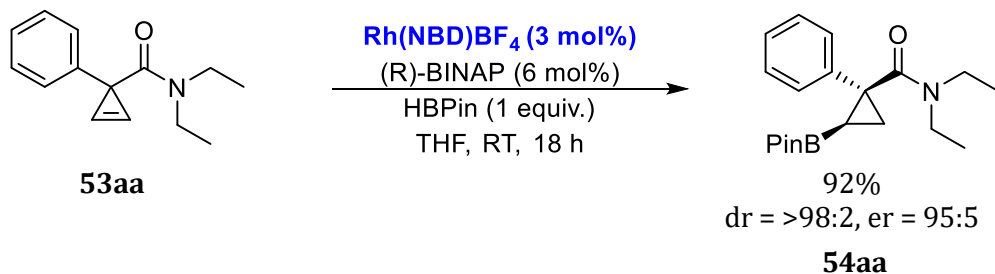
The proposed mechanism in **Scheme 17**, operating via cationic six coordinate rhodium(III) species **36**, is further supported by reactions carried out using AgOTf as halide scavenger (**Scheme 18a**) and cationic Rh(NBD)BF₄ as the source of rhodium (**Scheme 18b**). In both reactions, essentially the same yield and stereoselectivity was observed as when the reaction is run under standard conditions.

Scheme 18

a)



b)



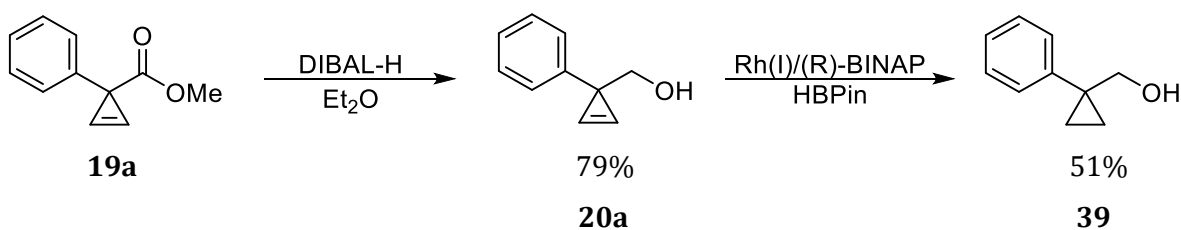
2.5 Evaluation of Alternative Directing Groups

One important implication of the proposed mechanistic rationale is the possible reversible interconversion between species **35** and **38**. It was speculated that the equilibrium between the two species could be influenced by incorporation of a directing group which would offer stronger coordination to the rhodium catalyst. Such substrate modification would shift the reaction

toward species **35** therefore reducing the feasibility of cycle II and increasing the overall diastereoselectivity of the catalytic process.

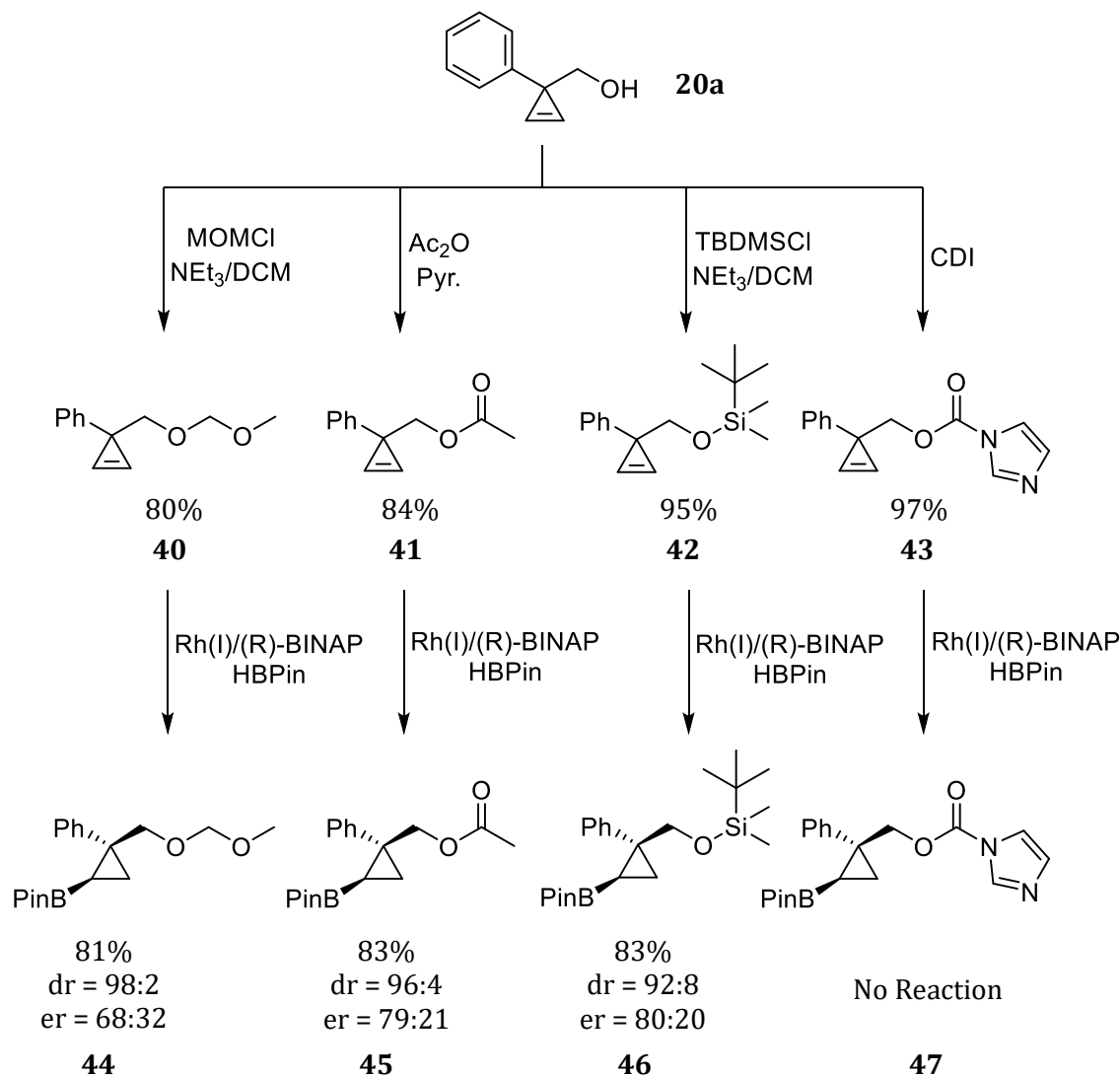
The evaluation of alternative directing groups began by first reducing the ester function of cyclopropene **19a** according to the protocol developed in chapter I (**Scheme 19**). The hydroxymethyl directing group proved to be incompatible with Rh(I)-catalyzed hydroboration. Cyclopropane **39**, which may have resulted from protonolysis of its corresponding cyclopropyl rhodium species **37**, was isolated from the reaction as the sole product.

Scheme 19



Alcohol **20a** was then further derivatized into four cyclopropenes bearing directing groups of varying strength which were subsequently subjected to optimized catalytic hydroboration conditions. (**Scheme 20**). Substrates bearing MOM ether **44**, acetate **45**, and TBDMS ether **46** were obtained in essentially equivalent chemical yield while diastereoselectivity seemed to decline with increasing steric size of the directing group. Enantioselectivities were disappointing in all examples. Carbamate **43** did not offer any reactivity and cyclopropene was recovered after prolonged exposure to hydroboration conditions.

Scheme 20

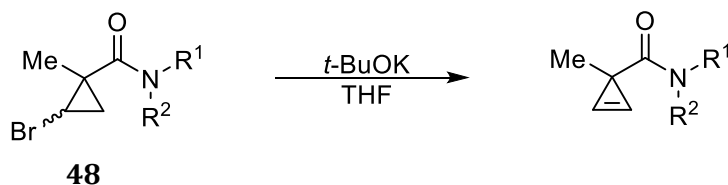


We next turned to the possibility of using an amide function to direct rhodium-catalyzed hydroboration due to previous reports detailing their use as efficient directors of alkali-metal assisted nucleophilic additions to cyclopropenes.^[36] However, protocols describing the construction of prochiral cyclopropenylcarboxamides with an unsubstituted double bond were sparse. One route to such structures involves the 1,2-dehydrobromination of

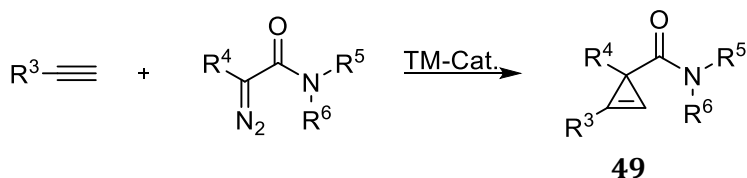
bromocyclopropanes^[36] **48** (**Scheme 21a**). However, this method has only been shown to be efficient with a methyl group at C-3 of cyclopropane. Another method is the catalytic cyclopropenation of terminal acetylenes with carbenoids generated from α -diazoacetamides^[37] (**Scheme 21b**). Once again, this method had severe limitations including having only been shown to be active toward the synthesis of cyclopropenes **49** possessing a substituted (R^3 = aryl, alkyl) double bond and with tertiary amides ($R^5, R^6 \neq H$)

Scheme 21

a)

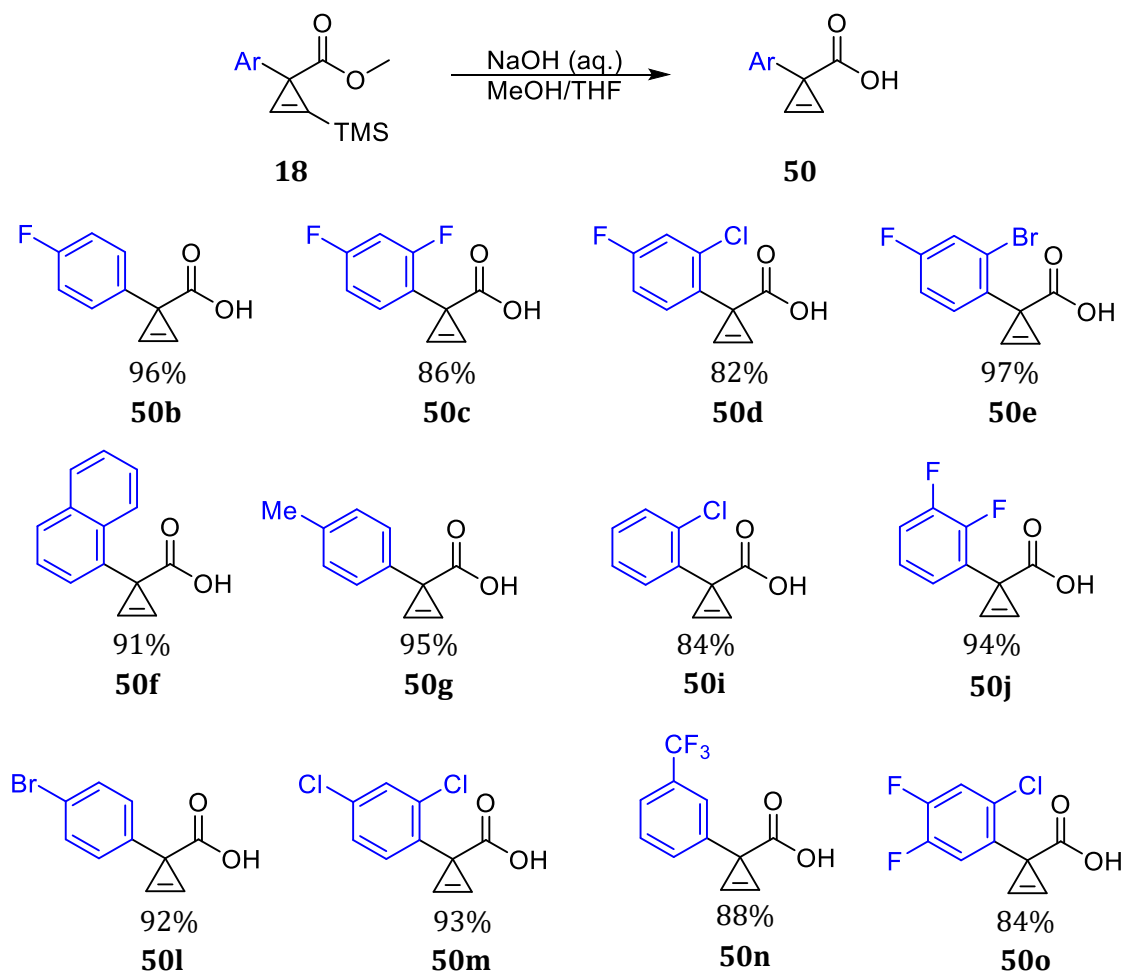


b)



Returning once again to the expedited Rh(II)-catalyzed cyclopropenation of TMS-acetylene with carbenoids generated from α -diazoacetates described in chapter I, we envisioned a more practical and direct conversion of cyclopropenecarboxylates **18** into their carboxamide analogs. It was quickly found that cyclopropenecarboxylates **18** could be very efficiently hydrolyzed to the corresponding desilylated carboxylic acids **50** under basic aqueous conditions without any noticeable degradation of the carbon-carbon double bond (**Table 12**).

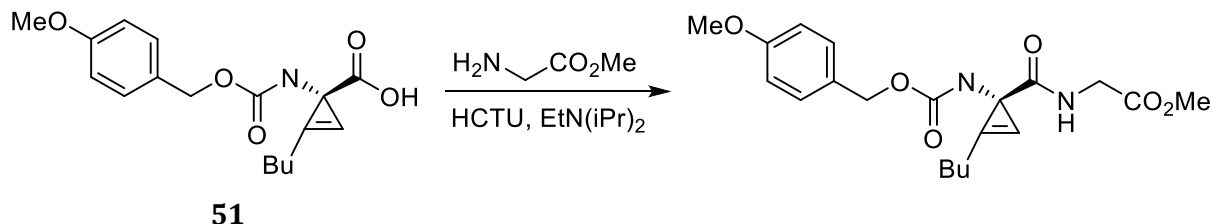
Table 12. One-pot desilylation/hydrolysis of TMS-protected cyclopropenylcarboxylates.



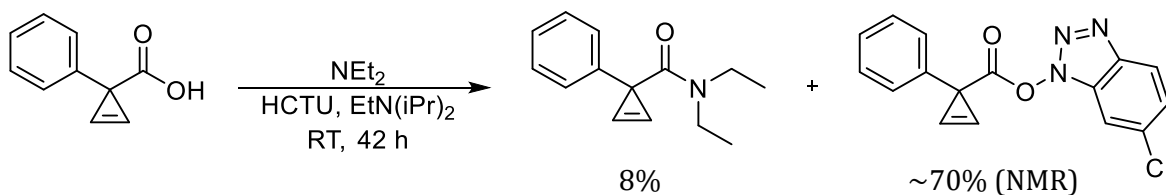
Fox^[38] had previously showed that an HCTU-promoted peptide coupling of substituted cyclopropene **51** was viable (**Scheme 22a**). However, attempts to adapt this protocol with an unsubstituted cyclopropene double bond provided poor results (**Scheme 22b**).

Scheme 22

a)



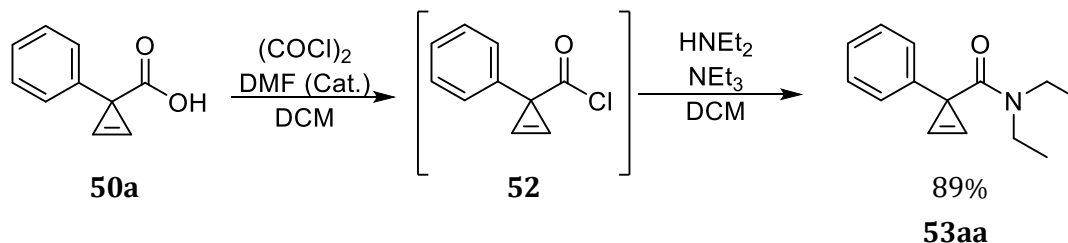
b)



Attempts to achieve direct peptide type coupling with alternative carboxylic acid activating reagents including DCC, EDC, HBTU, and CDI proved to be rather inefficient. Although conversion of the acid into the corresponding activated intermediate seemed to proceed relatively efficiently in all cases, the subsequent amine acylation step was rather sluggish and in many cases did not reach completion even after three days. This, along with the stoichiometric byproducts produced from these coupling reagents, led to significant complications during purification and to substantial product loss.

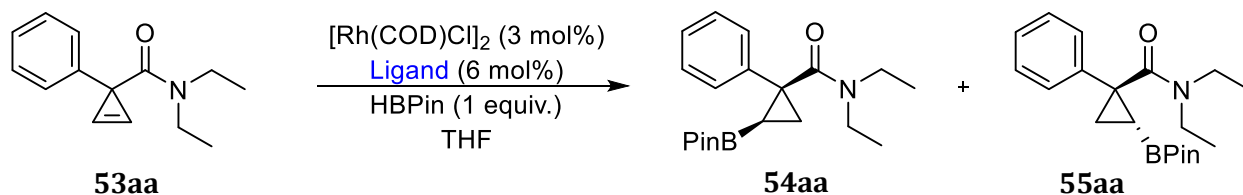
Next, coupling reagents which produce only gaseous byproducts were considered. Initial reactions performed with thionyl chloride and diethylamine provided mixtures of products along with significant decomposition. However, evaluation of more docile oxalyl chloride in the presence of catalytic DMF resulted in very efficient conversion of **50a** to the acyl chloride intermediate **52** (**Scheme 23**). This intermediate, without isolation or purification, was then exposed to diethylamine to provide cyclopropenylcarboxamide **53aa** as the sole product detectable by TLC and was able to be isolated in 89% yield (**Scheme 23**).

Scheme 23



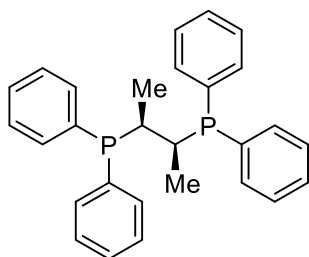
Substrate **53aa** was next subjected to standard directed asymmetric hydroboration conditions established for esters. We were pleased to find that the reaction was extremely diastereoselective although much slower than the comparable reaction directed by an ester function (**Table 13, entry 1**). Thus, reaction times were extended first to four hours and eventually overnight which allowed for complete conversion, 97% yield, and excellent diastereo- and enantioselectivity (**entries 2, 3**). For completeness, a variety of chiral ligands were also evaluated with three providing nearly equivalent reactivity (**entries 3, 8, 10**). However, due to our intentions of developing an economical and scalable reaction, we decided to proceed with BINAP due to its' wide availability and relatively low cost (**Table 13**).

Table 13. Optimization of directed CAHB of cyclopropenylamides.

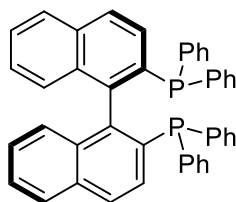


Entry	Ligand	Time, h ^[a]	Yield, % ^[b]	dr (54aa : 55aa) ^[c]	er ^[d]
1	(R)-BINAP	0.5	66	>98:2	ND
2	(R)-BINAP	4	81	>98:2	ND
3	(R)-BINAP	18	97	>98:2	96:4
4	(R)-Tol-BINAP	0.5	89	>98:2	97:3
5	(R)-DM-BINAP	4	90	>98:2	98:2
6	(R,R)-NORPHOS	2	96	>98:2	97:3
7	(S)-PHANEPHOS	1	86	>98:2	98:2
8	(S)-BINAPINE	0.5	99	>98:2	>99:1
9	(R)-BINAM	8	81	97:3	34:66
10	(S,S)-CHIRAPHOS	0.5	99	>98:2	3:97
11	(S,S)-Me-DUPHOS	2	80	98:2	82:12
12	(R,R,S,S)-DUANPHOS	18	73	>98:2	81:19
13	TaniaPhos SL-T001-1	42	27	95:5	ND
14	JosiPhos SL-J008-1	42	55	93:7	7:93

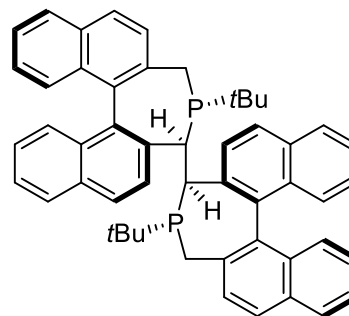
[a] Time for reaction to reach completion. [b] NMR yield of crude reaction mixtures using dibromomethane as standard. [c] Measured by NMR of crude reaction mixture, >98:2 indicates absence of minor isomer **55aa**. [d] Determined by chiral HPLC analysis.



(S,S)-CHIRAPHOS
\$175.71/mmol



(R)-BINAP
\$72.60/mmol



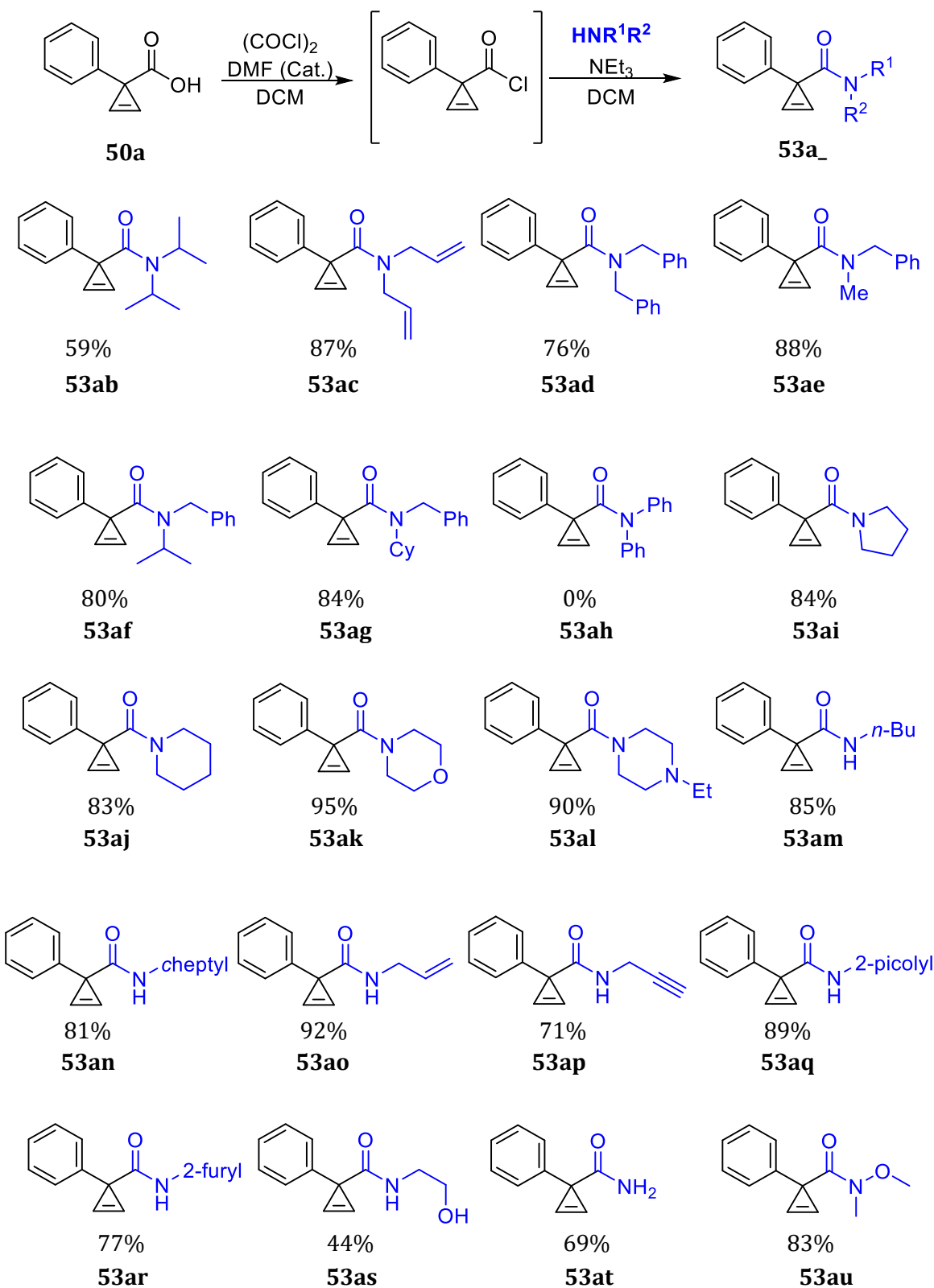
(S)-BINAPINE
\$1113.36/mmol

2.6 One-Pot Cyclopropenylamide Synthesis

With highly promising optimized conditions for amide directed asymmetric catalytic hydroboration in hand, the newly developed one-pot synthesis of prochiral cyclopropenylcarboxamides was thoroughly evaluated for compatibility and scope. First, the array of amines which could be acylated was evaluated (**Table 14**). As was expected, the reaction was very efficient with diallyl- and a variety of secondary benzylamines providing amides **53ac** and **53ad-53ag** in excellent yield. Diisopropylamine provided amide **53ab** in much lower yield most likely due to its greatly increased steric signature. Diphenylamide, **53ah**, proved to be incompatible with the acidic work up^[39], as complete hydrolysis was observed upon exposure to aqueous solution. Secondary cyclic amines including pyrrolidine **53ai**, piperidine **53aj**, morpholine **53ak**, and N-ethyl piperazine **53al** were efficiently transformed into the corresponding amides.

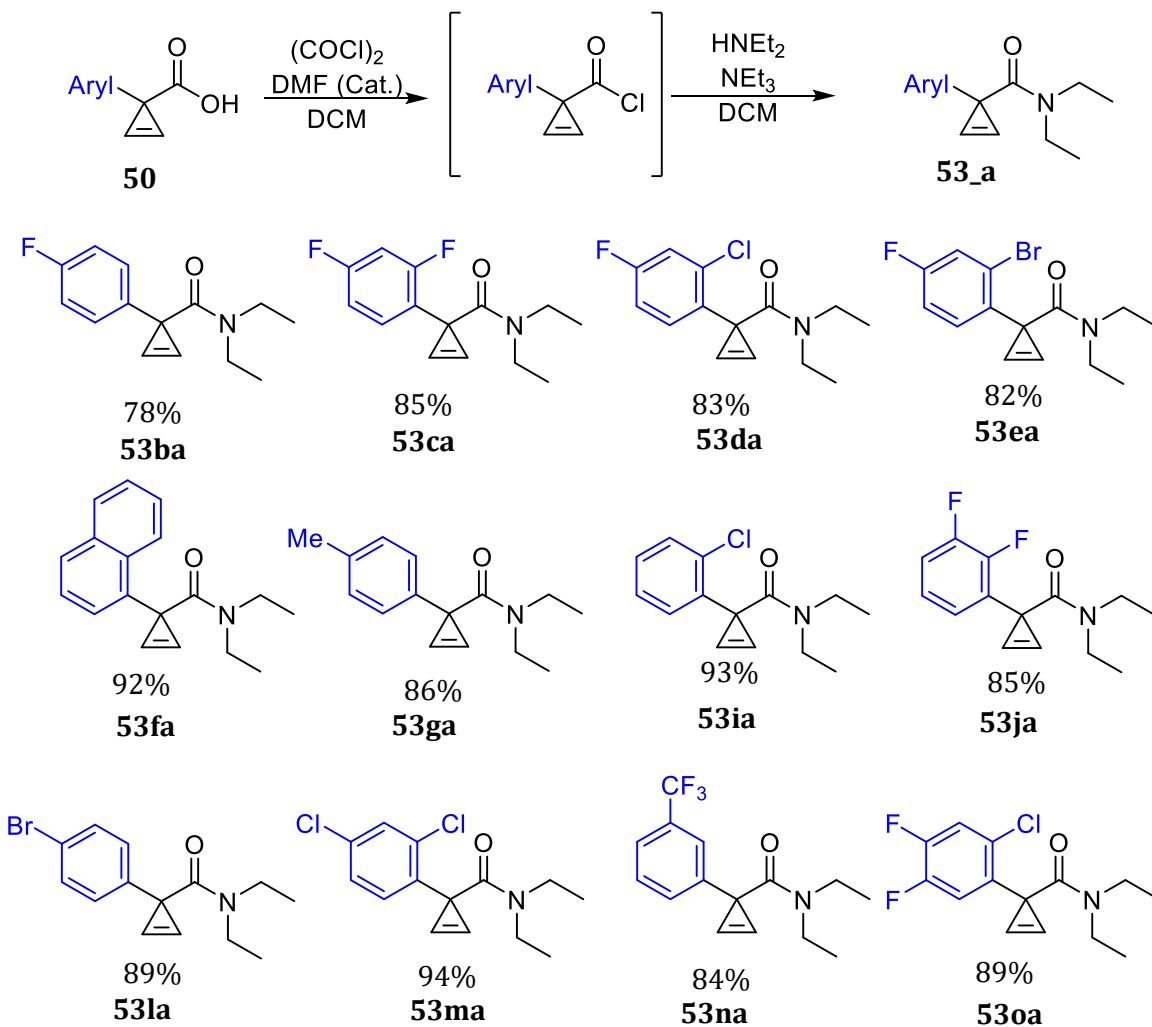
All primary amines evaluated reacted smoothly to provide secondary amides **53am-53ar**. Substrates **53aq** and **53ar** were obtained in good yield and are of particular interest for directed addition reactions due to the incorporation of an additional coordination point. Interestingly, amides **53as** and **53at** formed selectively when exposed to aqueous solutions of ethanolamine and ammonia respectively. The synthetically useful Weinreb amide **53au** could be accessed via acylation of N,O-dimethylhydroxylamine in good yield.

Table 14. Synthesis of cyclopropenylcarboxamides bearing variation on nitrogen atom.



Next, a series of diethylamides possessing the same set of aryl substituents as was evaluated in the directed catalytic asymmetric hydroboration of cyclopropenylcarboxylates, were synthesized in good yield (**Table 15**).

Table 15. Synthesis of cyclopropenylcarboxamides bearing variation on aryl ring.



2.7 Directed Catalytic Asymmetric Hydroboration of Cyclopropenylamides with Variation of Aryl Substituent

For direct comparison of amide against ester functions to direct catalytic asymmetric hydroboration, the series of carboxamide substrates shown in **Table 15** were evaluated under optimized hydroboration conditions (**Table 16**). All amides bearing mono-substituted aromatic rings provided cyclopropylboronates in high yields and as a single diastereomer although with slightly lower enantioselectivity than was observed with the comparable esters in **Table 11**. Interestingly, the most problematic substrates possessing multiple halogens, and specifically, 2-fluorinated aromatic rings **54ca** and **54ja**, showed great increases in diastereoselectivity, as all examples were obtained as a single diastereomeric product, exhibiting the superior directing ability of amides over the ester function. These very promising results prompted us to fully examine the ability of amides to direct Rh(I)-catalyzed hydroboration by screening various substitution patterns of the nitrogen atom of the directing group (**Table 17**).

Despite the increased steric hindrance of tertiary amides when compared to esters, all carboxamide directing groups evaluated proved to be highly diastereoselective as exemplified by dibenzylamide **54ad**. The excessively large diisopropylamide **54ab** exhibited fantastic facial selectivity but suffered slight reductions in yield and enantioselectivity. Cyclic amides **54ai** and **54ak** provided extremely high stereoselectivity but with a notable loss of yield, possibly due to the increased chelation of these directing groups to the rhodium transition metal. Finally, a Weinreb amide, was converted into cyclopropylboronate **54au** with a high degree of diastereo- and enantioselectivity.

Table 16. Directed CAHB of cyclopropenylamides with variation in aryl substituent.

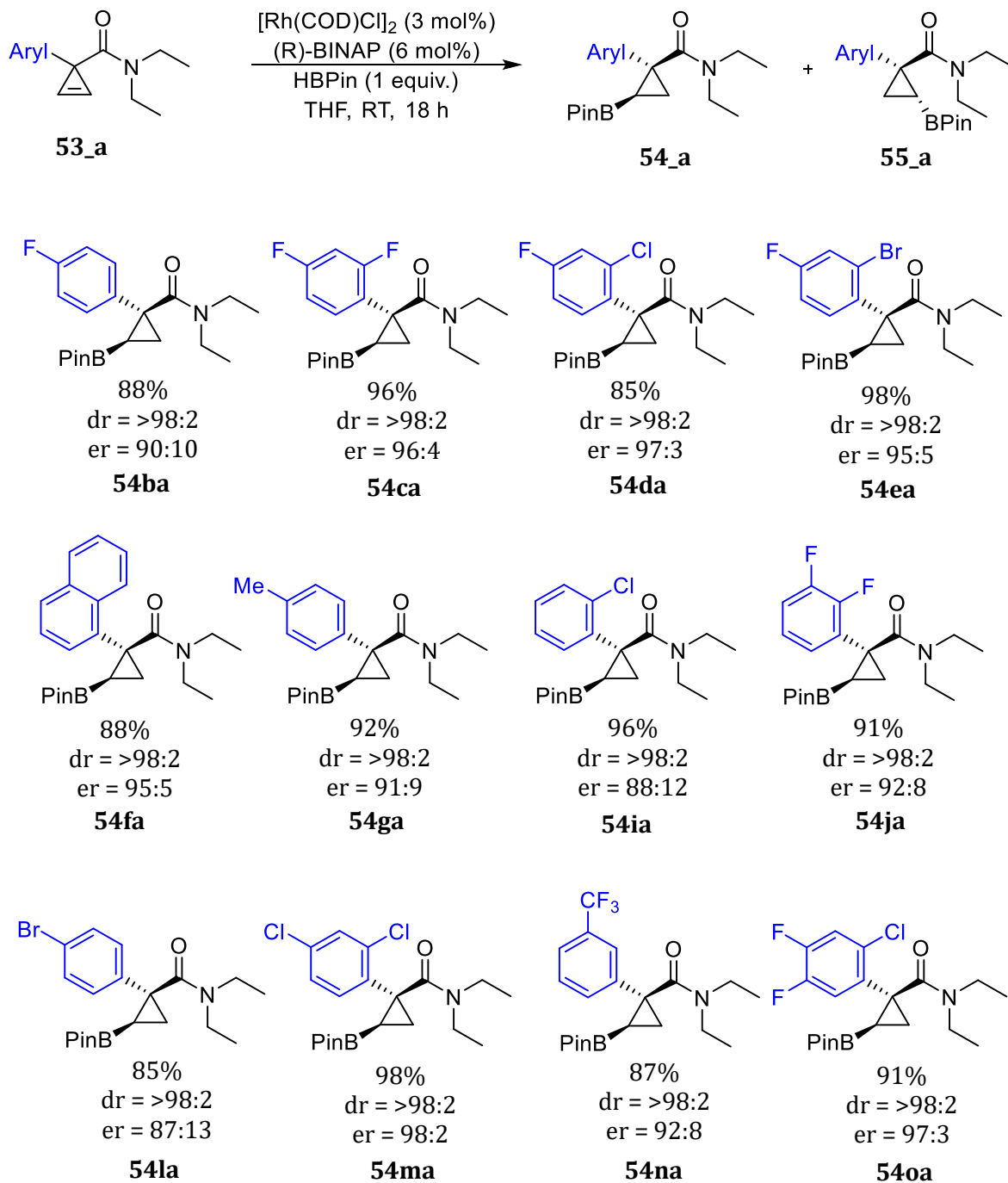
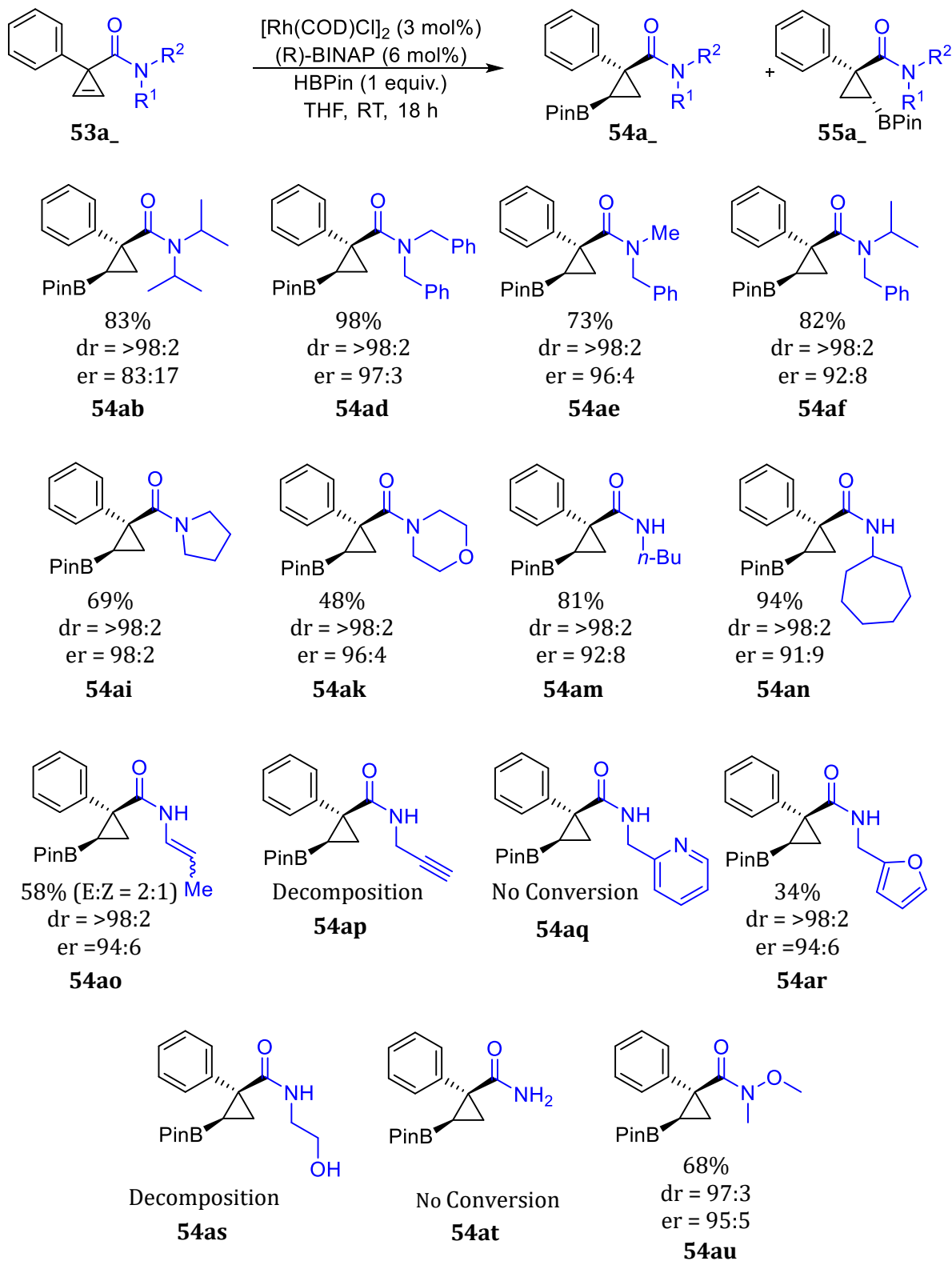


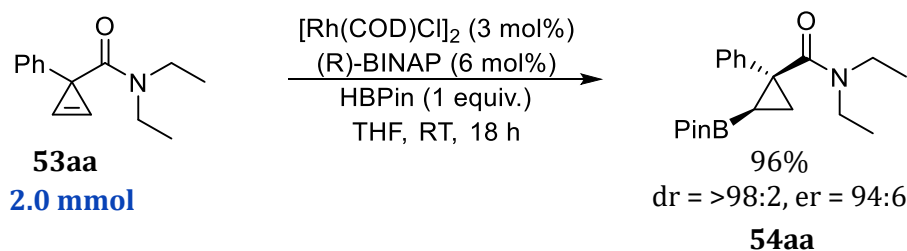
Table 17. Directed CAHB of cyclopropenylamides with variation at the nitrogen atom.



Less sterically demanding secondary amides **54am** and **54an** showed no reactivity with the relatively acidic N-H bond and were converted in high yield and selectivity. 2-furfuryl was a very effective directing group, but provided **54ar** in rather poor yield. Hydroboration providing **54ao** included a Rh-catalyzed migration of the double bond of allylamine to provide a 2:1 mixture of E and Z configured internal olefins. Substrates **54aq** and **54at** bearing very strongly chelating amides failed to undergo the intended transformation and were recovered from the reaction mixture. Additionally, the presence of an alcohol or triple bond proved incompatible, as **54as** and **54ap** resulted in only decomposition to a complex mixture of products.

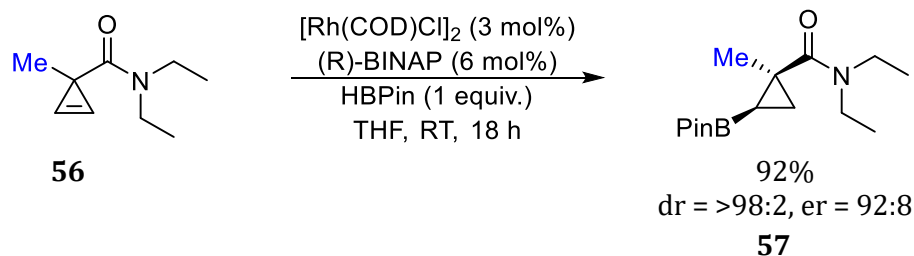
The hydroboration reaction proved to be equally efficient upon scale up to 6.5-fold (2.0 mmol). The preparative scale reaction provided cyclopropylboronate **54aa** in 96% yield and excellent diastereo- and enantioselectivity of >98:2 and 94:6 respectively (**Scheme 24**).

Scheme 24



Lastly, amide **56** bearing a methyl group on the opposing face of cyclopropene was evaluated and underwent highly stereoselective hydroboration in 92% yield (**Scheme 25**).

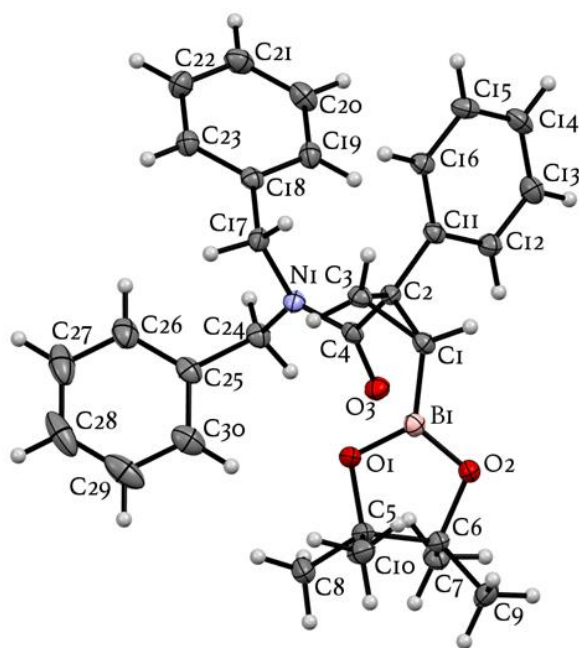
Scheme 25



2.8 Discussion of Origin and Determination of Absolute Configuration

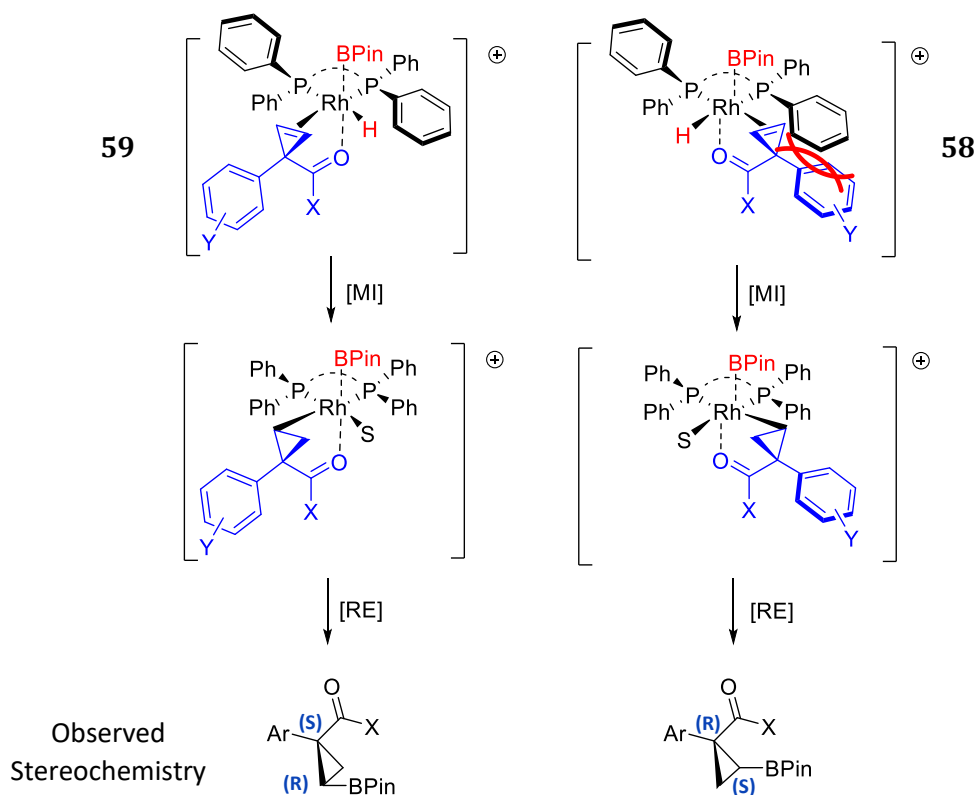
The absolute configuration of the obtained cyclopropylboronates was confirmed by X-ray analysis of dibenzyl- product **54ad** in which an (*S*)-configuration is observed at C2 and an (*R*)-configuration is observed at C1 of the cyclopropane ring (**Figure 5**).

Figure 5. ORTEP drawing of 54ad showing 50% probability amplitude displacement ellipsoids.



The observed enantioselectivity can be rationalized by the two ways cyclopropene could coordinate to the chiral transition metal. Coordination of cyclopropene as shown in right handed model **58**, would be expected to experience significant steric interactions between the aryl substituent of cyclopropene with the chiral phosphine ligand (**Scheme 26**). Therefore, it is believed cyclopropene would coordinate as is shown in structure **59**, which would then undergo diastereo- and enantiodefining hydorrhodation followed by reductive elimination to provide products with the configuration observed in **tables 11, 16, and 17**.

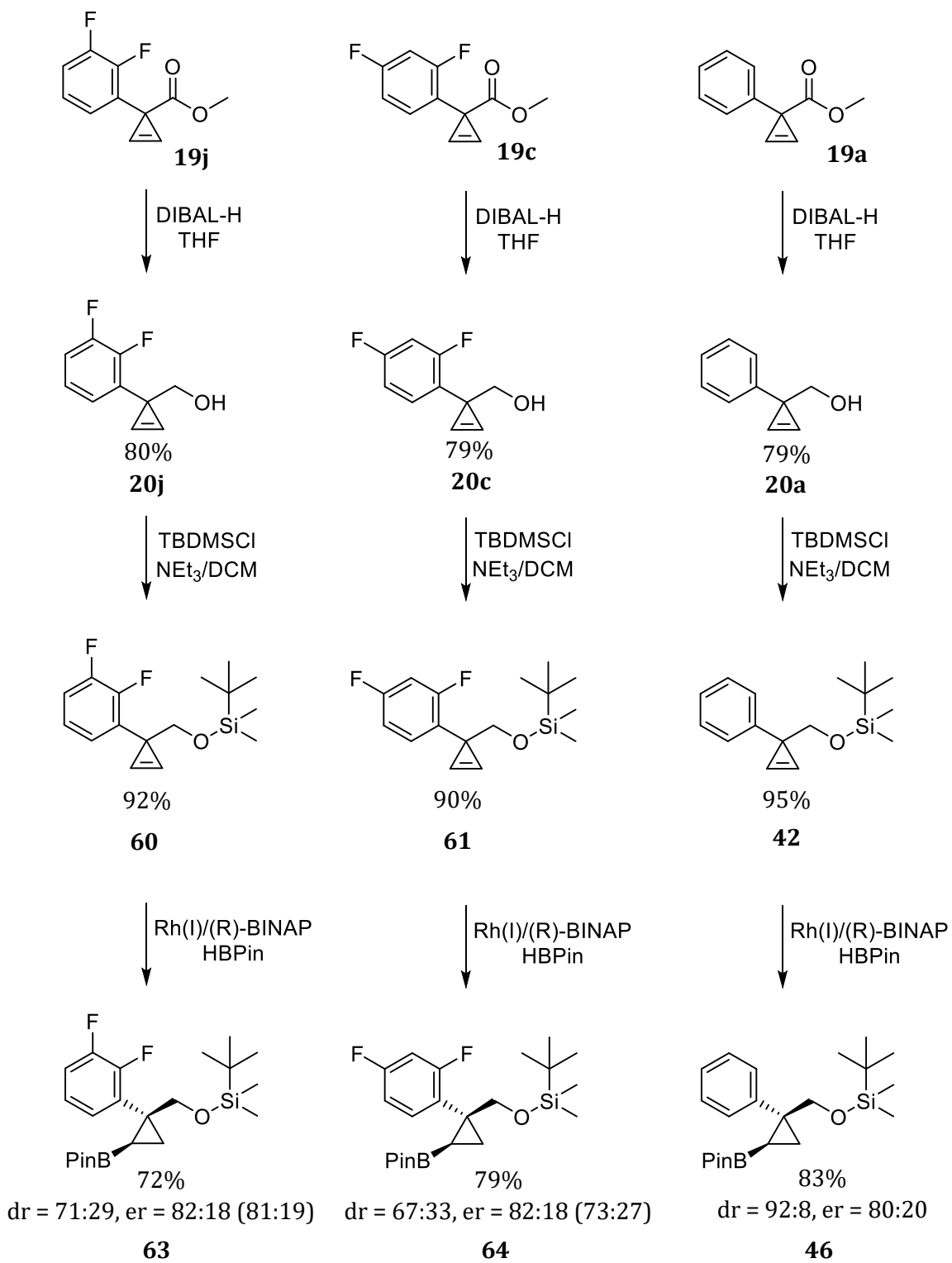
Scheme 26



2.9 Evaluation of *Ortho*-Fluoro-Effect

The possibility of influencing diastereoselectivity by enhancing the “*ortho*-fluoro” effect,^[34] which was observed in cyclopropenylcarboxylates bearing a fluorine in the 2-position of the aryl ring, became an interesting possibility. To test this idea, cyclopropenes **60** and **61** possessing relatively weakly directing^[40] *tert*-butyldimethylsilyl ether were synthesized by first reducing the ester using DIBAL-H followed by exposure of the alcohols to TBDMSCl under basic conditions (**Scheme 27**). Catalytic hydroboration was then conducted with each substrate to provide cyclopropylboronates **63** and **64**.

Scheme 27



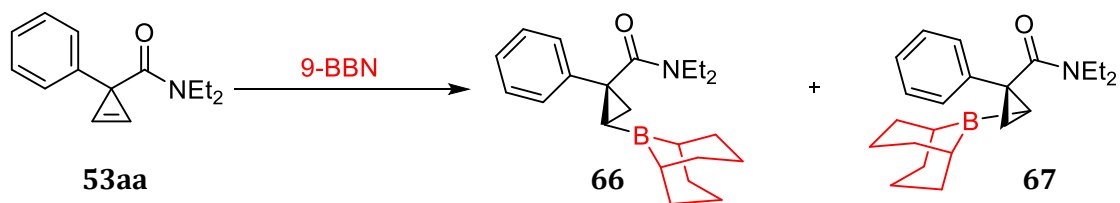
As expected, facial selectivities of *ortho*-fluorinated substrates **63** and **64** possessing *tert*-butyldimethylsilyl ether as a directing group were substantially lower than fluorine lacking example **46** (**Scheme 27**). This observation further supports the presence of a stabilizing *ortho-fluoro* effect, as was experienced during hydroboration of cyclopropenylcarboxylates. However, sufficient disruption of the directing groups' ability to deliver the transition metal to only one face of cyclopropene was not achieved, as the *cis*-configured **63** and **64** were still obtained as the major products.

2.10 Evaluation of Alternative Hydroboration Reagents

The possibility of utilizing other sources of boron was also investigated (**Scheme 28**). With 9-BBN the reaction proceeded with and without catalyst present and showed a preference for the non-directed diastereomer **67** in both cases (**Scheme 28a**). Without catalyst loaded in the reaction mixture, the products were obtained with a diastereomeric ratio of approximately 90:10, with each diastereomer remaining completely racemic. However, in the presence of catalyst, the diastereoselectivity declines to approximately 70:30, with the non-directed product remaining racemic while the directed product showed slight enantioenrichment. This leads us to believe that in addition to the direct background hydroboration of cyclopropene by 9-BBN,^[43] there is an asymmetric catalytic process occurring. Hydroboration conducted with catecholborane as the source of boron did not proceed without catalyst present and in the presence of catalyst fast and complete consumption of starting material was observed (**Scheme 28b**). However, cyclopropylboronates **68** were found to be very fragile and decomposed extremely rapidly.

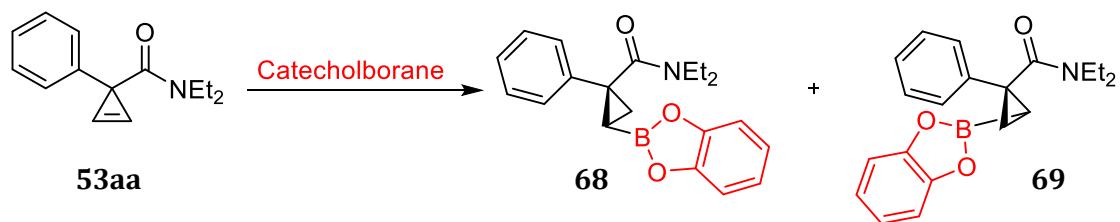
Scheme 28

a)



Rh(I)/(R)-BINAP	dr = 30 : 70 er = 73:27 : 50:50	} 59%
No Cat./No Lig.	dr = 13 : 87 er = 50:50 : 50:50	} 63%

b)



Rh(I)/(R)-BINAP 21% yield (NMR), Rapid Decomposition

No Cat./No Lig.

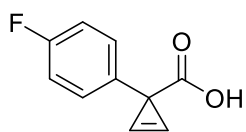
No Reaction

2.11 Conclusion

In conclusion, the directed Rh(I)-catalyzed asymmetric hydroboration of cyclopropenes has been extensively evaluated across a diverse array of prochiral substrates bearing the ester and amide functions as directing groups. The hydroboration of esters was found to be significantly more sensitive to the influence of the substituent on the opposing face of cyclopropene, especially ortho-fluorine atoms. However, utilization of the much more Lewis basic amide directing group, provided sufficient coordination to the transition metal to provide excellent yields and consistently high diastereo- and enantioselectivities across all substrates.

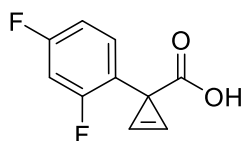
2.12 Experimental

2.12.1 Preparation of Cyclopropene Carboxylic Acids



1-(4-fluorophenyl)cycloprop-2-ene-1-carboxylic acid (**50b**)

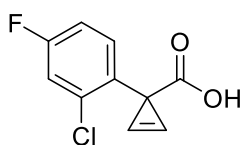
Typical Procedure: A solution of methyl 1-(4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18b**) (457 mg, 1.73 mmol, 1.0 equiv.) in a 1:1 mixture of methanol:tetrahydrofuran (20 mL) was stirred at 0 °C. A 1.5 M aqueous solution of sodium hydroxide (15 mL) was added dropwise and the mixture was stirred for 18 hours. Organic solvents were then removed under vacuum and the remaining aqueous solution was added to dichloromethane (20 mL). The mixture was acidified to pH 2 with 1N aqueous HCl. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 X 10 mL). The combined organic phases were washed with brine, dried with MgSO₄, filtered, and concentrated. The obtained product is typically pure enough to be used in further amide coupling as is, however, if necessary, further purification can be achieved by column chromatography on silica gel using a 1:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as colorless solid in 96% yield (289 mg, 1.66 mmol). *R*_f: 0.40; mp: 102.0 – 103.4 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.29 – 7.23 (m, 2H), 7.21 (s, 2H), 7.03 – 6.95 (m, 2H); ¹³C (126 MHz, CDCl₃): δ 181.3, 161.8 (d, *J* = 245.6 Hz), 136.5 (d, *J* = 3.2 Hz), 130.1 (+, d, *J* = 8.2 Hz, 2C), 115.1 (+, d, *J* = 21.5 Hz, 2C), 107.2 (+, 2C), 29.7; FTIR (KBr, cm⁻¹): 3155, 3114, 3072, 2972, 2846, 2619, 1693, 1650, 1604, 1512, 1427, 1317, 1222, 1161, 1108, 983, 933, 813, 752; HRMS (TOF ES): Found 177.0343, calculated for C₁₀H₆FO₂ (M-H) 177.0352 (5.1 ppm).



1-(2,4-difluorophenyl)cycloprop-2-ene-1-carboxylic acid (50c)

The titled compound was obtained via the typical procedure using methyl 1-(2,4-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate

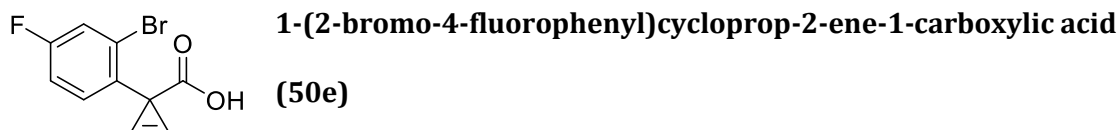
(18c) (488 mg, 1.73 mmol, 1.0 equiv.) as a pale yellow solid in 86% yield (280 mg, 1.43 mmol). mp: 98.7-101.8 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.02 (s, 2H), 6.88 (td, *J* = 8.4, 6.4 Hz, 1H), 6.60 – 6.48 (m, 2H); ¹³C (126 MHz, CDCl₃): δ 180.8, 162.3 (dd, *J* = 248.3, 11.9 Hz), 161.8 (dd, *J* = 249.3, 12.1 Hz), 131.0 (+, dd, *J* = 9.7, 5.6 Hz), 124.6 (dd, *J* = 15.8, 3.8 Hz), 111.3 (+, dd, *J* = 21.3, 3.7 Hz), 107.5 (+, d, *J* = 1.6 Hz, 2C), 104.1 (+, d, *J* = 25.5 Hz), 25.6; FTIR (KBr, cm⁻¹): 3178, 3134, 1693, 1661, 1614, 1504, 1421, 1269, 1138, 1088, 984, 854, 735, 636, 616; HRMS (TOF ES): Found 219.0223, calculated for C₁₀H₆F₂O₂Na (M+Na) 219.0234 (4.8 ppm).



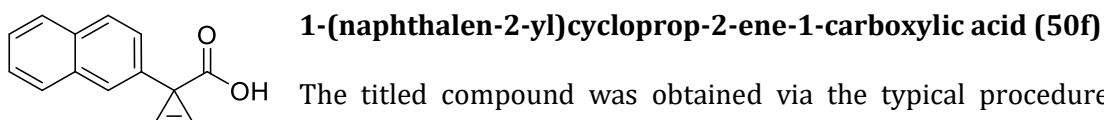
1-(2-chloro-4-fluorophenyl)cycloprop-2-ene-1-carboxylic acid (50d)

The titled compound was obtained via the typical procedure using methyl 1-(2-chloro-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate

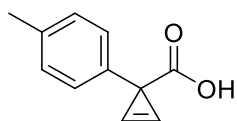
(18d) (517 mg, 1.73 mmol, 1.0 equiv.) as a colorless solid in 82% yield (303 mg, 1.43 mmol). mp: 152.4-155.1 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.30 (s, 2H), 7.18 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.09 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.93 (td, *J* = 8.3, 2.6 Hz, 1H); ¹³C (126 MHz, CDCl₃): δ 180.0, 161.8 (d, *J* = 249.3 Hz), 135.9 (d, *J* = 10.5 Hz), 135.4 (d, *J* = 3.7 Hz), 131.3 (+, d, *J* = 8.7 Hz), 117.0 (+, d, *J* = 24.8 Hz), 114.4 (+, d, *J* = 21.0 Hz), 108.2 (+, 2C), 29.3; FTIR (KBr, cm⁻¹): 3163, 3122, 1693, 1661, 1597, 1585, 1487, 1301, 1238, 1199, 1045, 982, 887, 856, 756, 634; HRMS (TOF ES): Found 210.9958, calculated for C₁₀H₅ClFO₂ (M-H) 210.9962 (1.9 ppm).



The titled compound was obtained via the typical procedure using methyl 1-(2-bromo-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18e**) (594 mg, 1.73 mmol, 1.0 equiv.) as colorless solid in 97% yield (430 mg, 1.67 mmol). *R_f*: 0.53; mp: 140 – 150 °C with decomposition; ¹H NMR (500 MHz, CDCl₃): δ 7.31 (s, 2H), 7.29 – 7.24 (m, 1H), 7.20 – 7.13 (m, 1H), 7.01 – 6.94 (m, 1H); ¹³C (126 MHz, CDCl₃): δ 180.5, 161.6 (d, *J* = 250.6 Hz), 137.1 (d, *J* = 3.7 Hz), 131.4 (+, d, *J* = 8.6 Hz), 125.3 (d, *J* = 9.9 Hz), 120.0 (+, d, *J* = 24.5 Hz), 114.9 (+, d, *J* = 21.0 Hz), 108.4(+, 2C), 31.4; FTIR (KBr, cm⁻¹): 3161, 3118, 2970, 2908, 1693, 1660, 1595, 1485, 1299, 1265, 1240, 1197, 1037, 981, 854, 754; HRMS (TOF ES): Found 254.9468, calculated for C₁₀H₅BrFO₂ (M-H) 254.9457 (4.3 ppm).

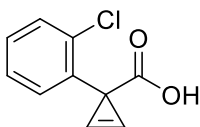


The titled compound was obtained via the typical procedure using methyl 1-(naphthalen-2-yl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18f**) (513 mg, 1.73 mmol, 1.0 equiv.) as a colorless solid in 91% yield (332 mg, 1.58 mmol). *R_f*: 0.27; mp: 188-190 °C (Decomposition); ¹H NMR (500 MHz, CDCl₃): δ 8.11 – 8.04 (m, 1H), 7.88 – 7.82 (m, 1H), 7.78 – 7.75 (m, 1H), 7.57 – 7.46 (m, 2H), 7.45 (s, 2H), 7.44 – 7.38 (m, 1H), 7.36 – 7.31 (m, 1H); ¹³C (126 MHz, CDCl₃): δ 181.8, 138.1, 133.8, 132.0, 128.9 (+), 128.2 (+), 126.3 (+), 126.0 (+), 125.9 (+), 125.8 (+), 124.3 (+), 108.8 (+, 2C), 29.1; FTIR (KBr, cm⁻¹): 3161, 3120, 3057, 1691, 1655, 1410, 1310, 1288, 1263, 1236, 1178, 1121, 955, 775, 733, 660, 640; HRMS (TOF ES): Found 233.0590, calculated for C₁₄H₁₀O₂Na (M+Na) 233.0579 (4.9 ppm).



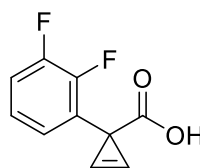
1-(p-tolyl)cycloprop-2-ene-1-carboxylic acid (50g)

The titled compound was obtained via the typical procedure using methyl 1-(p-tolyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18g**) (450 mg, 1.73 mmol, 1.0 equiv.) as colorless solid in 95% yield (286 mg, 1.64 mmol). *R*_f: 0.47; mp: 105.7 – 106.4 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.21 (s, 2H), 7.20 – 7.16 (m, 2H), 7.14 – 7.09 (m, 2H), 2.32 (s, 3H); ¹³C (126 MHz, CDCl₃): δ 181.5, 137.7, 136.6, 129.0 (+, 2C), 128.3 (+, 2C), 107.4 (+, 2C), 30.0, 21.2 (+); FTIR (KBr, cm⁻¹): 3155, 3114, 3018, 2920, 1691, 1649, 1514, 1413, 1313, 1290, 1257, 1236, 977, 954, 941, 929, 867, 813, 740, 628; HRMS (TOF ES): Found 173.0596, calculated for C₁₁H₉O₂ (M-H) 173.0603 (4.0 ppm).



1-(2-chlorophenyl)cycloprop-2-ene-1-carboxylic acid (50i)

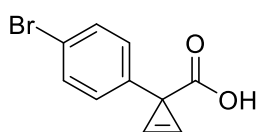
The titled compound was obtained via the typical procedure using methyl 1-(2-chlorophenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18i**) (486 mg, 1.73 mmol, 1.0 equiv.) as colorless solid in 84% yield (284 mg, 1.46 mmol). *R*_f: 0.47; mp: 144.9 - 147.3 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.35 – 7.32 (m, 1H), 7.31 (s, 2H), 7.22 – 7.19 (m, 3H); ¹³C (126 MHz, CDCl₃): δ 180.7, 139.3, 135.1, 130.3 (+), 129.6 (+), 128.8 (+), 127.2 (+), 108.2 (+, 2C), 29.9; FTIR (KBr, cm⁻¹): 3163, 3120, 2972, 1693, 1660, 1473, 1438, 1411, 1294, 1265, 1226, 1056, 981, 945, 873, 750, 730, 702, 649; HRMS (TOF ES): Found 193.0062, calculated for C₁₀H₆ClO₂ (M-H) 193.0056 (3.1 ppm).



1-(2,3-difluorophenyl)cycloprop-2-ene-1-carboxylic acid (50j)

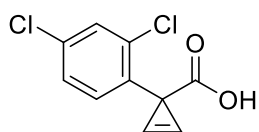
The titled compound was obtained via the typical procedure using methyl 1-(2,3-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18j**) (488 mg, 1.73 mmol, 1.0 equiv.) as colorless solid in 94% yield (319 mg, 1.63 mmol). *R*_f: 0.47; mp:

115.1 – 116.3 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.27 (s, 2H), 7.10 – 6.97 (m, 2H), 6.95 – 6.88 (m, 1H); ^{13}C (126 MHz, CDCl_3): δ 180.5, 150.6 (dd, J = 248.3, 12.9 Hz), 149.8 (dd, J = 248.2, 12.7 Hz), 130.9 (d, J = 12.3 Hz), 124.9 (+, t, J = 3.1 Hz), 124.1 (+, dd, J = 6.9, 4.6 Hz), 116.4 (+, d, J = 17.2 Hz), 107.3 (+, d, J = 1.7 Hz, 2C), 25.8 (t, J = 2.6 Hz); FTIR (KBr, cm^{-1}): 3163, 3122, 2977, 2914, 2837, 2651, 2540, 1697, 1660, 1589, 1481, 1425, 1313, 1274, 1253, 1220, 1118, 1037, 991, 952, 864, 810, 742; HRMS (TOF ES): Found 195.0259, calculated for $\text{C}_{10}\text{H}_5\text{F}_2\text{O}_2$ (M-H) 195.0258 (0.5 ppm).



1-(4-bromophenyl)cycloprop-2-ene-1-carboxylic acid (50l)

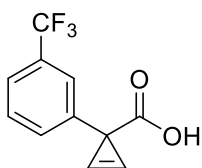
The titled compound was obtained via the typical procedure using methyl 1-(4-bromophenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18l**) (764 mg, 2.35 mmol, 1.0 equiv.) as colorless solid in 92% yield (519 mg, 2.17 mmol). R_f : 0.47; mp: 125.7 – 126.5 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.46 – 7.39 (m, 2H), 7.19 (s, 2H), 7.19 – 7.14 (m, 2H); ^{13}C (126 MHz, CDCl_3): δ 181.1, 139.7, 131.4 (+, 2C), 130.2 (+, 2C), 120.9, 106.9 (+, 2C), 29.9; FTIR (KBr, cm^{-1}): 3126, 3110, 3047, 2962, 2881, 1691, 1658, 1485, 1415, 1394, 1307, 1222, 1072, 975, 871, 813, 761, 692; HRMS (TOF ES): Found 236.9539, calculated for $\text{C}_{10}\text{H}_6\text{BrO}_2$ (M-H) 236.9551 (5.1 ppm).



1-(2,4-dichlorophenyl)cycloprop-2-ene-1-carboxylic acid (50m)

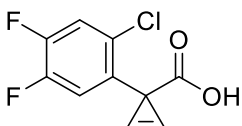
The titled compound was obtained via the typical procedure using methyl 1-(2,4-dichlorophenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18m**) (545 mg, 1.73 mmol, 1.0 equiv.) as colorless solid in 93% yield (369 mg, 1.61 mmol). R_f : 0.53; mp: 135.5 – 137.9 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.36 (d, J = 2.1 Hz, 1H), 7.29 (s, 2H), 7.19 (dd, J = 8.2, 2.1 Hz, 1H), 7.13 (d, J = 8.2 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 180.2, 137.9, 135.9, 133.9, 131.2 (+), 129.4 (+), 127.5 (+), 108.0 (+, 2C), 29.4; FTIR (KBr, cm^{-1}): 3166, 3114, 2962, 2894, 1697, 1662,

1587, 1473, 1419, 1296, 1263, 1224, 1099, 1056, 981, 933, 804, 744, 611; HRMS (TOF ES): Found 226.9662, calculated for $C_{10}H_5Cl_2O_2$ (M-H) 226.9667 (2.2 ppm).



1-(3-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylic acid (50n)

The titled compound was obtained via the typical procedure using methyl 1-(3-(trifluoromethyl)phenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18n**) (759 mg, 2.40 mmol, 1.0 equiv.) as colorless solid in 88% yield (483 mg, 2.12 mmol). *R_f*: 0.53; mp: 104.3 – 105.5 °C; 1H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.47 (m, 3H), 7.46 – 7.39 (m, 1H), 7.24 (s, 2H); ^{13}C (126 MHz, $CDCl_3$): δ 180.8, 141.6, 132.0 (+), 130.6 (q, J = 32.1 Hz), 128.7 (+), 125.3 (+, d, J = 4.0 Hz), 124.2 (q, J = 273.4 Hz), 123.8 (+, d, J = 3.9 Hz), 106.8 (2C), 30.1; FTIR (KBr, cm^{-1}): 3128, 3043, 2979, 2950, 2927, 2837, 1693, 1666, 1427, 1334, 1222, 1166, 1134, 1074, 987, 933, 806, 750, 705; HRMS (TOF ES): Found 227.0313, calculated for $C_{11}H_6F_3O_2$ (M-H) 227.0320 (3.1 ppm).

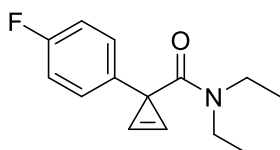


1-(2-chloro-4,5-difluorophenyl)cycloprop-2-ene-1-carboxylic acid (50o)

The titled compound was obtained via the typical procedure using methyl 1-(2-chloro-4,5-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-ene-1-carboxylate (**18o**) (546 mg, 1.73 mmol, 1.0 equiv.) as colorless solid in 84% yield (336 mg, 1.46 mmol). *R_f*: 0.50; mp: 131.1 – 133.9 °C; 1H NMR (500 MHz, $CDCl_3$): δ 7.28 (s, 2H), 7.18 (dd, J = 9.9, 7.2 Hz, 1H), 7.02 (dd, J = 10.3, 8.1 Hz, 1H); ^{13}C (126 MHz, $CDCl_3$): δ 180.6, 149.5 (dd, J = 251.8, 13.6 Hz), 149.2 (dd, J = 249.6, 12.6 Hz), 137.7 – 134.6 (m), 129.9 (dd, J = 8.0, 3.5 Hz), 118.8 (+, d, J = 18.1 Hz), 118.6 (+, d, J = 20.2 Hz), 107.8 (+, 2C), 29.5; FTIR (KBr, cm^{-1}): 3166, 3120, 3072, 2979, 2837, 1697, 1666, 1600, 1496, 1417, 1396,

1307, 1280, 1172, 939, 879, 794, 742; HRMS (TOF ES): Found 228.9871, calculated for $C_{10}H_4ClF_2O_2$ (M-H) 228.9868 (1.3 ppm).

2.12.2 One-Pot Cyclopropene Amide Synthesis

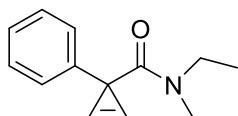


N,N-diethyl-1-(4-fluorophenyl)cycloprop-2-ene-1-carboxamide
(53ba)

Typical Procedure: Part 1: 1-(4-fluorophenyl)cycloprop-2-ene-1-carboxylic acid (**50b**) (223 mg, 1.28 mmol, 1.0 equiv.) and dimethylformamide (2 drops) were dissolved in freshly distilled and dried dichloromethane (7 mL) and added to a flame dried round bottom flask under an inert nitrogen atmosphere. Oxalyl chloride (200 μ L, 297 mg, 2.34 mmol, 1.5 equiv.) was then added slowly dropwise and stirred at room temperature for 2 hours. The solution was then evaporated under reduced pressure to provide a pale yellow solid material.

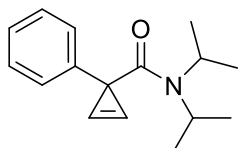
Part 2: diethylamine (323 μ L, 228 mg, 3.12 mmol, 2.0 equiv.) and triethylamine (436 μ L, 316 mg, 3.12 mmol, 2.0 equiv.), and freshly dried dichloromethane (3 mL) were combined in a flame dried two neck round bottom flask under an inert nitrogen atmosphere. Recovered material from part 1 was dissolved in freshly dried dichloromethane (3 mL) and added to the two neck flask slowly dropwise. The reaction was then stirred for 18 hours and then partitioned between water and dichloromethane. The aqueous phase was then acidified using 1N HCl to a pH of approximately 2. The organic phase was then extracted with properly acidified water (pH=2, 3 x 10mL). The combined acidic aqueous layers were then back extracted once with dichloromethane which was combined with other organic layers, washed with brine, dried, filtered, and concentrated. The product was then purified by silica gel column chromatography using a 2:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 78% yield (232 mg, 0.099

mmol). *R*_f: 0.23; mp: 86.7 – 88.7 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.25 (s, 2H), 7.12 – 7.05 (m, 2H), 6.99 – 6.93 (m, 2H), 3.38 (q, *J* = 7.1 Hz, 2H), 3.30 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 173.0, 161.6 (d, *J* = 244.9 Hz), 139.4 (d, *J* = 3.1 Hz), 127.6 (+, d, *J* = 8.1 Hz, 2C), 115.3 (+, d, *J* = 21.5 Hz, 2C), 109.9 (+, 2C), 41.9 (-), 39.1 (-), 31.6, 13.8 (+), 12.7 (+); FTIR (KBr, cm⁻¹): 3070, 2975, 2935, 2875, 1620, 1508, 1460, 1429, 1380, 1363, 1313, 1276, 1220, 1159, 1120, 1097, 1012, 825, 810; HRMS (TOF ES): Found 256.1121, calculated for C₁₄H₁₆FNONa (M+Na) 256.1114 (2.7 ppm).



N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (53aa)

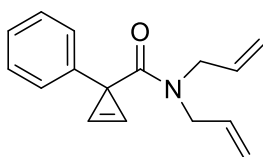
The titled compound was obtained via typical procedure using 1-phenylcycloprop-2-ene-1-carboxylic acid (**50a**) (250 mg, 1.56 mmol, 1.0 equiv.) as a colorless solid in 89% yield (300 mg, 1.39 mmol). *R*_f: 0.16, mp: 84.5-86.0 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.33 – 7.10 (m, 7H), 3.40 (q, *J* = 7.0 Hz, 2H), 3.32 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 173.2, 143.5, 128.3 (2C, +), 126.2 (+), 125.9 (2C, +), 109.6 (2C, +), 41.9 (-), 38.9 (-), 32.0, 13.7 (+), 12.6 (+); FTIR (KBr, cm⁻¹): 3078, 2972, 2934, 2872, 1624, 1491, 1472, 1429, 1379, 1364, 1277, 1221, 1121, 1076, 1018, 999, 839, 764, 739, 700, 638; HRMS (TOF ES): Found 215.1311, calculated for C₁₄H₁₇NO (M+) 215.1310 (0.5 ppm).



N,N-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (53ab)

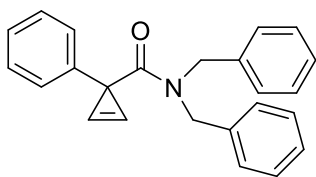
Compound was obtained via typical procedure using diisopropylamine (438 μL, 316 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 3:1 hexane:ethyl acetate mobile phase to provide the titled compound as a very pale yellow solid in 59% yield (224 mg, 0.92 mmol). *R*_f: 0.26; mp: 66.9-68.2 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.24 – 7.19 (m, 2H), 7.18 (s, 2H), 7.14 – 7.07 (m, 3H), 4.23

(h, $J = 6.7$ Hz, 1H), 3.22 (h, $J = 6.8$ Hz, 1H), 1.40 (d, $J = 6.8$ Hz, 6H), 0.84 (d, $J = 6.7$ Hz, 6H); ^{13}C (126 MHz, CDCl_3): δ 173.2, 143.7, 128.3 (+, 2C), 126.3 (+), 126.1 (+, 2C), 110.0 (+, 2C), 49.5 (+), 45.6 (+), 33.5, 20.5 (+, 2C), 20.4 (+, 2C); FTIR (KBr, cm^{-1}): 3080, 3061, 2999, 2966, 2932, 1643, 1626, 1614, 1493, 1435, 1369, 1329, 1213, 1161, 1045, 739, 700, 667, 621; HRMS (TOF ES): Found 244.1701, calculated for $\text{C}_{16}\text{H}_{22}\text{NO}$ ($\text{M}+\text{H}$) 244.1701 (0.0 ppm).



N,N-diallyl-1-phenylcycloprop-2-ene-1-carboxamide (53ac)

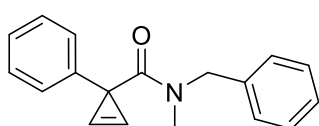
Compound was obtained via typical procedure using diallylamine (385 μL , 363 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 3:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 87% yield (324 mg, 1.35 mmol). R_f : 0.22; mp: 43.1-44.2 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3): δ 7.25 – 7.19 (m, 2H), 7.18 (s, 2H), 7.16 – 7.11 (m, 1H), 7.09 – 7.05 (m, 2H), 5.74 (ddt, $J = 17.1, 10.2, 6.1$ Hz, 1H), 5.39 (ddt, $J = 17.2, 10.8, 5.4$ Hz, 1H), 5.13 – 4.89 (m, 4H), 3.92 (d, $J = 6.1$ Hz, 2H), 3.81 (d, $J = 5.4$ Hz, 2H); ^{13}C (126 MHz, CDCl_3): δ 173.9, 143.2, 133.4 (+), 133.0 (+), 128.5 (+, 2C), 126.5 (+), 126.0 (+, 2C), 117.7 (-), 117.5 (-), 109.6 (+, 2C), 49.5 (-), 46.7 (-), 31.9; FTIR (KBr, cm^{-1}): 3082, 3022, 2982, 2918, 1645, 1634, 1614, 1493, 1447, 1412, 1285, 1248, 995, 926, 764, 733, 700; HRMS (TOF ES): Found 240.1387, calculated for $\text{C}_{16}\text{H}_{18}\text{NO}$ ($\text{M}+\text{H}$) 240.1388 (0.4 ppm).



N,N-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (53ad)

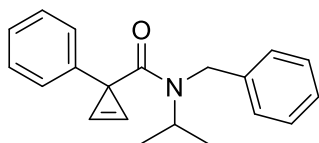
Compound was obtained via typical procedure using dibenzylamine (600 μL , 616 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 3:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 76% yield (402 mg, 1.18 mmol). R_f : 0.30; mp:

112.3-113.9 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.27 – 7.13 (m, 10H), 7.12 – 7.07 (m, 1H), 7.05 (s, 2H), 7.05 – 7.02 (m, 2H), 6.88 – 6.84 (m, 2H), 4.47 (s, 2H), 4.31 (s, 2H); ^{13}C (126 MHz, CDCl_3): δ 174.6, 143.1, 137.3, 136.9, 128.9 (+, 2C), 128.8 (+, 2C), 128.7 (+, 2C), 128.6 (+, 2C), 127.6 (+), 127.6 (+), 127.0 (+, 2C), 126.6 (+), 126.1 (+, 2C), 109.8 (+, 2C), 50.2 (-), 47.5 (-), 32.0; FTIR (KBr, cm^{-1}): 3084, 3061, 3028, 2924, 2870, 1645, 1634, 1495, 1452, 1418, 1229, 1080, 957, 752, 735, 698, 654; HRMS (TOF ES): Found 340.1701, calculated for $\text{C}_{24}\text{H}_{22}\text{NO}$ (M+H) 340.1701 (0.0 ppm).



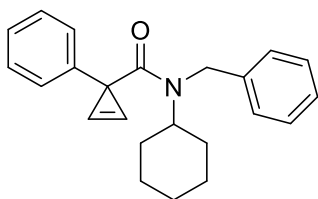
N-benzyl-N-methyl-1-phenylcycloprop-2-ene-1-carboxamide
(53ae)

Compound was obtained via typical procedure using N-methylbenzylamine (403 μL , 378 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 3:1 hexane:ethyl acetate mobile phase to provide the titled compound as a mixture of rotomers in a ratio of 1.3:1 as a colorless liquid in 88% yield (362 mg, 1.37 mmol). R_f : 0.15; ^1H NMR (500 MHz, CDCl_3): δ [7.36 – 7.11 (m), Σ 10H], [7.29, (s) & 7.14 (s), Σ 2H], [4.63 (s) & 4.51 (s), Σ 2H], [2.92 (s) & 2.80 (s), Σ 3H]; ^{13}C (126 MHz, CDCl_3): δ Major Rotomer: 174.0, 143.0, 137.3, 128.6 (+, 2C), 128.5 (+, 2C), 128.2 (+, 2C), 127.4 (+), 126.3 (+), 125.9 (+, 2C), 109.4 (+, 2C), 50.7 (-), 34.9 (+), 32.1 . Minor Rotomer: 174.6, 143.1, 136.8, 128.8 (+, 2C), 128.5 (+, 2C), 127.5 (+), 126.7 (+, 2C), 126.5 (+), 125.9 (+, 2C), 109.4 (+, 2C), 53.6 (-), 33.1 (+), 31.8; FTIR (KBr, cm^{-1}): 3084, 3028, 2920, 1645, 1614, 1489, 1447, 1398, 1269, 1101, 1003, 959, 739, 698, 652; HRMS (TOF ES): Found 264.1392, calculated for $\text{C}_{18}\text{H}_{18}\text{NO}$ (M+H) 264.1388 (1.4 ppm).



N-benzyl-N-isopropyl-1-phenylcycloprop-2-ene-1-carboxamide (53af)

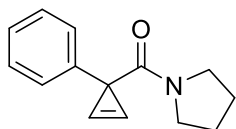
Compound was obtained via typical procedure using N-isopropylbenzylamine (522 μ L, 466 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 3:1 hexane:ethyl acetate mobile phase to provide the titled compound as a mixture of rotomers in a ratio of 1.3:1 as a colorless solid in 80% yield (363 mg, 1.25 mmol). *R*_f: 0.23; mp: 58.7-60.3 °C; ¹H NMR (500 MHz, CDCl₃): δ [7.33 (s) & 6.83 (s), Σ 2H], [7.32 – 7.27 (m), Σ 5H], [7.25 – 7.17 (m), Σ 3H] [7.11 – 7.01 (m), Σ 2H], [4.69 (h, *J* = 6.8 Hz) & 4.48 (h, *J* = 6.7 Hz), Σ 1H], [4.52 (s) & 4.37 (s), Σ 2H], [1.16 (d, *J* = 6.8 Hz) & 0.92 (d, *J* = 6.8 Hz), Σ 6H]; ¹³C (126 MHz, CDCl₃): δ Major Rotomer: 174.4, 143.4, 139.9, 128.5 (+, 2C), 128.4 (+, 2C), 127.5 (+, 2C), 126.7 (+), 126.5 (+), 126.2 (+, 2C), 110.2 (+, 2C), 49.3 (+), 43.9 (-), 32.4, 21.4 (+, 2C). Minor Rotomer: 174.7, 143.4, 139.5, 128.6 (+, 2C), 128.5 (+, 2C), 127.2 (+), 126.6 (+, 2C), 126.4 (+), 125.9 (+, 2C), 109.3 (+, 2C), 47.7 (-), 47.1 (+), 32.8, 20.3 (+, 2C); FTIR (KBr, cm⁻¹): 3082, 3061, 3026, 2972, 2932, 1626, 1495, 1437, 1412, 1339, 1178, 1078, 735, 698, 652; HRMS (TOF ES): Found 292.1692, calculated for C₂₀H₂₂NO (M+H) 292.1701 (3.2 ppm).



N-benzyl-N-cyclohexyl-1-phenylcycloprop-2-ene-1-carboxamide (53ag)

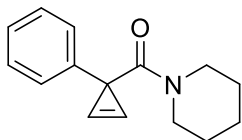
Compound was obtained via typical procedure using N-cyclohexylbenzylamine (591 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 3:1 hexane:ethyl acetate mobile phase to provide the titled compound as a mixture of rotomers in a ratio of 1.5:1 as a very pale yellow oil in 84% yield (432 mg, 1.30 mmol). *R*_f: 0.27; ¹H NMR (500 MHz, CDCl₃): δ [7.35 (s) & 6.80 (s), Σ 2H], [7.32 – 7.27 (m), Σ 5H], [7.25 – 7.18 (m), Σ 3H], [7.09 – 7.00 (m), Σ 2H], [4.52 (s) & 4.40 (s), Σ 2H], [4.46 – 4.40 (m) &

4.07 – 3.97 (m), Σ 1H], [1.82 – 1.69 (m) & 1.65 – 1.56 (m) & 1.52 – 1.44 (m) & 1.40 – 1.22 (m) & 1.08 – 0.84 (m), Σ 10H]; ^{13}C (126 MHz, CDCl_3): δ Major Rotomer: 174.6, 143.5, 139.9, 128.5 (+, 2C), 128.3 (+, 2C), 127.5 (+, 2C), 126.7 (+), 126.6 (+), 126.3 (+, 2C), 110.7 (+, 2C), 58.1 (+), 44.9 (-), 32.6, 32.1 (-, 2C), 26.1 (-, 2C), 25.3 (-). Minor Rotomer: 174.7, 143.5, 139.8, 128.5, 128.5, 127.1, 126.6, 126.4, 125.9, 109.2, 54.9, 47.9, 32.7, 30.6, 26.0, 25.6; FTIR (KBr, cm^{-1}): 3082, 3060, 3028, 2930, 2854, 1645, 1625, 1607, 1495, 1447, 1416, 1244, 1078, 1003, 912, 737, 698, 656; HRMS (TOF ES): Found 332.2015, calculated for $\text{C}_{23}\text{H}_{26}\text{NO}$ (M+H) 332.2014 (0.2 ppm).



(1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (53ai)

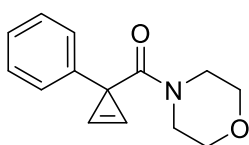
Compound was obtained via typical procedure using pyrrolidine (256 μL , 222 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 2:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 84% yield (279 mg, 1.31 mmol). R_f : 0.10; mp: 140.7-143.6 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3): δ 7.25 – 7.20 (m, 2H), 7.20 (s, 2H), 7.15 – 7.10 (m, 1H), 7.09 – 7.05 (m, 2H), 3.45 (dd, J = 7.2, 6.2 Hz, 2H), 3.15 (dd, J = 6.4 Hz, 2H), 1.79 – 1.67 (m, 4H); ^{13}C (126 MHz, CDCl_3): δ 172.4, 143.0, 128.5 (+, 2C), 126.3 (+), 126.2 (+, 2C), 109.3 (+, 2C), 46.6 (-), 45.9 (-), 32.9, 26.1 (-), 24.2 (-); FTIR (KBr, cm^{-1}): 3103, 3057, 2968, 2872, 1616, 1447, 1431, 1045, 914, 731, 681, 669; HRMS (TOF ES): Found 214.1234, calculated for $\text{C}_{14}\text{H}_{16}\text{NO}$ (M+H) 214.1232 (0.9 ppm).



(1-phenylcycloprop-2-en-1-yl)(piperidin-1-yl)methanone (53aj)

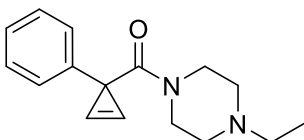
Compound was obtained via typical procedure using piperidine (308 μL , 266 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 2:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 83% yield (295 mg, 1.30 mmol). R_f : 0.26; mp: 128.6-132.5 $^{\circ}\text{C}$; ^1H

NMR (500 MHz, CDCl₃): δ 7.31 – 7.24 (m, 2H), 7.22 (s, 2H), 7.20 – 7.16 (m, 1H), 7.14 – 7.11 (m, 2H), 3.63 – 3.51 (m, 2H), 3.46 – 3.22 (m, 2H), 1.69 – 1.45 (m, 4H), 1.36 – 1.18 (m, 2H); ¹³C (126 MHz, CDCl₃): δ 172.3, 143.5, 128.4 (+, 2C), 126.2 (+), 125.9 (+, 2C), 109.2 (+, 2C), 47.0 (-), 42.7 (-), 31.8, 26.0 (-), 25.5 (-), 24.5 (-); FTIR (KBr, cm⁻¹): 3103, 3059, 3016, 2943, 2916, 2851, 1618, 1439, 1269, 1256, 1122, 1043, 974, 910, 852, 760, 739, 696, 681; HRMS (TOF ES): Found 228.1386, calculated for C₁₅H₁₈NO (M+H) 228.1388 (0.9 ppm).



morpholino(1-phenylcycloprop-2-en-1-yl)methanone (53ak)

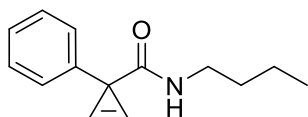
Compound was obtained via typical procedure using morpholine (270 μ L, 272 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 2:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 95% yield (340 mg, 1.48 mmol). *R*_f: 0.13; mp: 115.1-117.6 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.32 – 7.27 (m, 2H), 7.23 (s, 2H), 7.22 – 7.17 (m, 1H), 7.14 – 7.09 (m, 2H), 3.65 (s, 4H), 3.39 (s, 4H); ¹³C (126 MHz, CDCl₃): δ 172.7, 142.9, 128.6 (+, 2C), 126.6 (+), 125.8 (+, 2C), 108.9 (+, 2C), 66.8 (-), 66.5 (-), 46.4 (-), 42.1 (-), 31.5; FTIR (KBr, cm⁻¹): 3105, 3063, 2966, 2916, 2856, 1626, 1429, 1273, 1248, 1115, 980, 766, 737, 702; HRMS (TOF ES): Found 230.1197, calculated for C₁₄H₁₆NO₂ (M+H) 230.1181 (6.9 ppm).



(4-ethylpiperazin-1-yl)(1-phenylcycloprop-2-en-1-yl)methanone (53al)

Titled compound was obtained via typical procedure (part 1). For part 2: 1-ethylpiperazine (396 μ L, 356 mg, 3.12 mmol, 2.0 equiv.) and triethylamine (436 μ L, 316 mg, 3.12 mmol, 2.0 equiv.), and freshly dried dichloromethane (3.0 mL) were combined in a flame dried two neck round bottom flask under an inert nitrogen atmosphere. Recovered material from

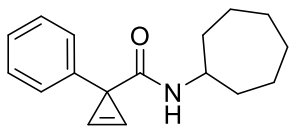
part 1 was dissolved in freshly dried dichloromethane (3 mL) and added to the two neck flask slowly dropwise. The reaction was then stirred for 18 hours and then partitioned between water and dichloromethane. The aqueous phase was then acidified using 1N HCl to a pH of approximately 2. The organic phase was then extracted with properly acidified water (pH=2, 3 x 15 mL). The pH of the combined aqueous layers was then adjusted to approximately 9 with saturated sodium bicarbonate and extracted with dichloromethane (3 x 15 mL). The combined organic phase was then washed with brine, dried, filtered, and concentrated. The product was then purified by trimethylamine neutralized silica gel column chromatography using an ethyl acetate mobile phase to provide the titled compound as a colorless solid in 90% yield (361 mg, 1.41 mmol). *R*_f: 0.17; mp: 51.9-53.7 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.29 – 7.23 (m, 2H), 7.20 (s, 2H), 7.19 – 7.14 (m, 1H), 7.11 – 7.07 (m, 2H), 3.70 – 3.61 (m, 2H), 3.45 – 3.37 (m, 2H), 2.44 – 2.36 (m, 2H), 2.33 (q, *J* = 7.2 Hz, 2H), 2.19 – 2.08 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 172.4, 143.1, 128.4 (+, 2C), 126.4 (+), 125.9 (+, 2C), 108.9 (+, 2C), 52.6 (-), 52.4 (-), 52.2 (-), 45.8 (-), 41.6 (-), 31.6, 11.9 (+); FTIR (KBr, cm⁻¹): 3080, 2968, 2931, 2808, 1628, 1437, 1252, 1167, 1124, 1022, 982, 764, 737, 700, 652; HRMS (TOF ES): Found 257.1648, calculated for C₁₆H₂₁N₂O (M+H) 257.1654 (2.3 ppm).



N-butyl-1-phenylcycloprop-2-ene-1-carboxamide (53am)

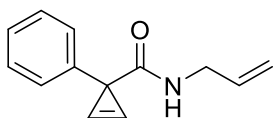
Compound was obtained via typical procedure using butylamine (308 μL, 228 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 85% yield (284 mg, 1.32 mmol). *R*_f: 0.32; mp: 48.2-50.1 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.35 – 7.21 (m, 5H), 7.25 (s, 2H), 5.60 (s, 1H), 3.21 (td, *J* = 7.2, 5.8 Hz, 2H), 1.48 – 1.31 (m, 2H), 1.31 – 1.15 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 174.8, 142.0,

128.8 (+, 2C), 128.6 (+, 2C), 127.1 (+), 108.9 (+, 2C), 39.9 (-), 32.6, 31.7 (-), 20.0 (-), 13.8 (+); FTIR (KBr, cm^{-1}): 3277, 3082, 2952, 2927, 2858, 1623, 1541, 1431, 1308, 1224, 1143, 1012, 743, 694, 689; HRMS (TOF ES): Found 216.1396, calculated for $\text{C}_{14}\text{H}_{18}\text{NO}$ ($\text{M}+\text{H}$) 216.1388 (3.5 ppm).



N-cycloheptyl-1-phenylcycloprop-2-ene-1-carboxamide (53an)

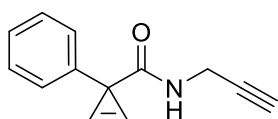
Compound was obtained via typical procedure using cycloheptylamine (397 μL , 353 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 81% yield (321 mg, 1.26 mmol). R_f : 0.42; mp: 118.9-120.8 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3): δ 7.35 – 7.22 (m, 5H), 7.25 (s, 2H), 5.52 (d, J = 7.7 Hz, 1H), 4.07 – 3.81 (m, 1H), 1.90 – 1.76 (m, 2H), 1.62 – 1.37 (m, 8H), 1.38 – 1.27 (m, 2H); ^{13}C (126 MHz, CDCl_3): δ 173.6, 142.1, 128.8 (+, 2C), 128.7 (+, 2C), 127.1 (+), 108.9 (+, 2C), 50.9 (+), 35.0 (-, 2C), 32.7, 27.9 (-, 2C), 24.1 (-, 2C); FTIR (KBr, cm^{-1}): 3294, 3136, 3084, 2914, 2853, 1614, 1531, 1445, 1319, 1627, 1334, 1009, 739, 696, 667; HRMS (TOF ES): Found 256.1702, calculated for $\text{C}_{17}\text{H}_{22}\text{NO}$ ($\text{M}+\text{H}$) 256.1701 (0.2 ppm).



N-allyl-1-phenylcycloprop-2-ene-1-carboxamide (53ao)

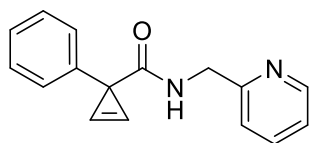
Compound was obtained via typical procedure using allylamine (233 μL , 178 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 92% yield (286 mg, 1.44 mmol). R_f : 0.27; mp: 68.0-69.1 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3): δ 7.38 – 7.21 (m, 5H), 7.28 (s, 2H), 5.78 (ddt, J = 17.3, 10.6, 5.5 Hz, 1H), 5.68 (s, 1H), 5.15 – 5.00 (m, 2H), 3.91 – 3.82 (m, 2H); ^{13}C (126 MHz, CDCl_3): δ 174.8, 141.8, 134.4 (+), 128.9 (+, 2C), 128.7 (+, 2C), 127.3 (+), 116.0 (-), 108.9 (+, 2C), 42.5 (-), 32.6; FTIR (KBr, cm^{-1}): 3279, 3080,

2927, 1626, 1529, 1425, 1265, 1146, 1013, 986, 916, 741, 694; HRMS (TOF ES): Found 200.1077, calculated for $C_{13}H_{14}NO$ (M+H) 200.1075 (0.8 ppm).



**1-phenyl-N-(prop-2-yn-1-yl)cycloprop-2-ene-1-carboxamide
(53ap)**

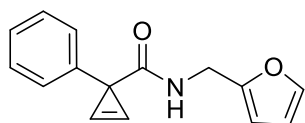
Compound was obtained via typical procedure using propargylamine (200 μ L, 172 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 71% yield (219 mg, 1.11 mmol). R_f : 0.33; mp: 123.8-124.7 $^{\circ}C$; 1H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 7.31 (s, 2H), 5.78 (s, 1H), 4.07 (dd, J = 5.4, 2.6 Hz, 2H), 2.20 (t, J = 2.6 Hz, 1H); ^{13}C (126 MHz, $CDCl_3$): δ 174.8, 141.4, 129.1 (+, 2C), 128.8 (+, 2C), 127.5 (+), 108.7 (+, 2C), 79.8 (+), 71.5, 32.5, 29.9 (-); FTIR (KBr, cm^{-1}): 3319, 3286, 3134, 3090, 1655, 1630, 1524, 1423, 1360, 1277, 1005, 930, 854, 744, 675, 635; HRMS (TOF ES): Found 198.0922, calculated for $C_{13}H_{12}NO$ (M+H) 198.0919 (1.6 ppm).



1-phenyl-N-(pyridin-2-ylmethyl)cycloprop-2-ene-1-carboxamide (53aq)

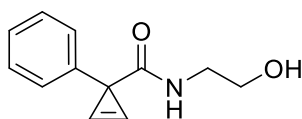
Compound was obtained via typical procedure (part 1). For part 2: 2-(aminomethyl)pyridine (322 μ L, 337 mg, 3.12 mmol, 2.0 equiv.) and triethylamine (436 μ L, 316 mg, 3.12 mmol, 2.0 equiv.), and freshly dried dichloromethane (3.0 mL) were combined in a flame dried two neck round bottom flask under an inert nitrogen atmosphere. Recovered material from part 1 was dissolved in freshly dried dichloromethane (3 mL) and added to the two neck flask slowly dropwise. The reaction was then stirred for 18 hours and then partitioned between water and dichloromethane. The aqueous phase was then acidified using 1N HCl to a pH of

approximately 2. The organic phase was then extracted with properly acidified water (pH=2, 3 x 15 mL). The pH of the combined aqueous layers was then adjusted to approximately 9 with saturated sodium bicarbonate and extracted with dichloromethane (3 x 15 mL). The combined organic phase was then washed with brine, dried, filtered, and concentrated. The product was then purified by trimethylamine neutralized silica gel column chromatography using a 1:3 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 89% yield (349 mg, 1.39 mmol). *R*_f: 0.23; mp: 97.7-100.2 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.53 – 8.40 (m, 1H), 7.75 – 7.63 (m, 1H), 7.37 – 7.26 (m, 6H), 7.33 (s, 2H), 7.23 – 7.19 (m, 1H), 6.82 (s, 1H), 4.58 (d, *J* = 5.4 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 175.4, 156.7, 148.3 (+), 141.7, 137.7 (+), 128.9 (+, 2C), 128.8 (+, 2C), 127.3 (+), 122.7 (+), 122.6, 109.1 (+, 2C), 45.0 (-), 32.5; FTIR (KBr, cm⁻¹): 3290, 3084, 3061, 1660, 1643, 1634, 1514, 1494, 1435, 1296, 1252, 995, 756, 700, 667; HRMS (TOF ES): Found 251.1185, calculated for C₁₆H₁₅N₂O (M+H) 251.1184 (0.2 ppm).



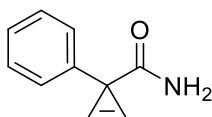
N-(furan-2-ylmethyl)-1-phenylcycloprop-2-ene-1-carboxamide
(53ar)

Compound was obtained via typical procedure using furfurylamine (276 µL, 303 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 77% yield (286 mg, 1.20 mmol). *R*_f: 0.33; mp: 51.4-54.1 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.36 – 7.22 (m, 6H), 7.27 (s, 2H), 6.28 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.16 (dd, *J* = 3.2, 0.9 Hz, 1H), 5.92 (t, *J* = 5.7 Hz, 1H), 4.43 (dd, *J* = 5.6, 0.8 Hz, 2H); ¹³C (126 MHz, CDCl₃): δ 174.8, 151.6, 142.1 (+), 141.6, 128.9 (+, 2C), 128.7 (+, 2C), 127.3 (+), 110.4 (+), 108.8 (+, 2C), 107.2 (+), 37.2 (-), 32.6; FTIR (KBr, cm⁻¹): 3292, 3107, 3082, 3057, 1637, 1504, 1445, 1294, 1229, 1148, 1076, 1007, 741, 700, 663; HRMS (TOF ES): Found 240.1026, calculated for C₁₅H₁₄NO₂ (M+H) 240.1025 (0.4 ppm).



**N-(2-hydroxyethyl)-1-phenylcycloprop-2-ene-1-carboxamide
(53as)**

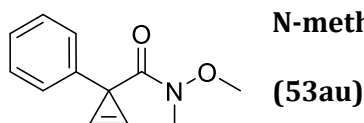
Compound was obtained via typical procedure using ethanolamine (189 μ L, 190 mg, 3.12 mmol, 2.0 equiv.). The product was then purified by silica gel column chromatography using an ethyl acetate mobile phase to provide the titled compound as a colorless oil in 44% yield (138 mg, 0.68 mmol). *R*_f: 0.17; ¹H NMR (500 MHz, CDCl₃): δ 7.17 – 7.05 (m, 5H), 7.08 (s, 2H), 5.92 (s, 1H), 3.44 (t, *J* = 5.5 Hz, 2H), 3.18 (td, *J* = 5.7, 4.4 Hz, 2H), 2.88 (s, 1H); ¹³C (126 MHz, CDCl₃): δ 176.7, 141.5, 129.0 (+, 2C), 128.8 (+, 2C), 127.4 (+), 108.9 (+, 2C), 62.7 (-), 43.3 (-), 32.5; FTIR (KBr, cm⁻¹): 3340, 3103, 2934, 2876, 1660, 1643, 1614, 1537, 1518, 1445, 1240, 1072, 991, 764, 700, 665; HRMS (TOF ES): Found 204.1030, calculated for C₁₂H₁₄NO₂ (M+H) 204.1025 (2.7 ppm).



1-phenylcycloprop-2-ene-1-carboxamide (53at)

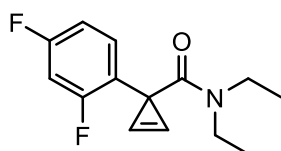
Compound was obtained via typical procedure (part 1). In part 2, the recovered acyl chloride from part 1 was dissolved in tetrahydrofuran (3 mL) and added slowly dropwise to a solution of approximately 30% aqueous ammonia (5 mL) and stirred overnight. The mixture was then concentrated, added to water (10 mL), and then extracted with ethyl acetate (3 x 10 mL). Combined organic phases were then washed with brine, dried, filtered, and concentrated. The product was then purified by silica gel column chromatography using an ethyl acetate mobile phase to provide the titled compound as a colorless solid in 69% yield (171 mg, 1.07 mmol). *R*_f: 0.23; mp: 118.2-119.0 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.32 – 7.16 (m, 5H), 7.22 (s, 2H), 5.98 (s, 1H), 5.54 (s, 1H); ¹³C (126 MHz, CDCl₃): δ 178.0, 141.7, 129.0 (+, 2C), 128.7 (+, 2C), 127.4 (+), 108.7 (+, 2C), 32.2 ; FTIR (KBr, cm⁻¹): 3362, 3188, 3111, 1608, 1402, 1261, 1113, 993,

760, 737, 696, 642; HRMS (TOF ES): Found 160.0754, calculated for C₁₀H₁₀NO (M+H) 160.0762 (5.0 ppm).



N-methoxy-N-methyl-1-phenylcycloprop-2-ene-1-carboxamide

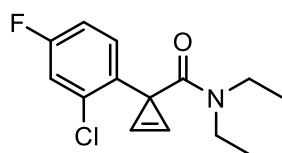
Compound was obtained via typical procedure using N,O-dimethylhydroxylamine (228 mg, 2.34 mmol, 1.50 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 83% yield (262 mg, 1.29 mmol). *R*_f: 0.30; mp: 74.3-75.6 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.29 (s, 2H), 7.28 – 7.25 (m, 2H), 7.22 – 7.13 (m, 3H), 3.30 (s (broad), 3H), 3.15 (s, 3H); ¹³C (126 MHz, CDCl₃): δ 175.3, 143.2, 128.3 (+, 2C), 126.3 (+, 3C), 109.9 (+, 2C), 60.7 (+), 32.8, 31.7 (+); FTIR (KBr, cm⁻¹): 3080, 3018, 2972, 2937, 1649, 1624, 1491, 1423, 1387, 1200, 1026, 966, 756, 729, 702, 648; HRMS (TOF ES): Found 204.1031, calculated for C₁₂H₁₄NO₂ (M+H) 204.1025 (3.2 ppm).



1-(2,4-difluorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (53ca)

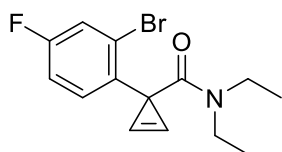
Compound was obtained via typical procedure A using 1-(2,4-difluorophenyl)cycloprop-2-ene-1-carboxylic acid (**50c**) (163 mg, 0.831 mmol, 1.0 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a very light brown solid in 85% yield (178 mg, 0.708 mmol). *R*_f: 0.26; mp: 59.7-60.8 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.34 (s, 2H), 7.16 (td, *J* = 8.8, 6.4 Hz, 1H), 6.84 – 6.78 (m, 1H), 6.77 – 6.72 (m, 1H), 3.44 – 3.23 (m, 4H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 173.0, 161.7 (dd, *J* = 248.3, 11.9 Hz), 161.2 (dd, *J* = 249.8, 11.8 Hz), 130.4 (+, dd, *J* = 9.6, 5.5 Hz), 126.8 (dd, *J* = 12.6, 3.8 Hz), 111.4 (+, dd, *J* = 21.1, 3.7

Hz), 110.3 (+, d, J = 1.9 Hz, 2C), 104.2 (+, t, J = 25.6 Hz), 41.7 (-), 39.6 (-), 27.8, 13.3 (+), 12.5 (+); FTIR (KBr, cm^{-1}): 3080, 2976, 2935, 2876, 1625, 1500, 1421, 1267, 1140, 1092, 974, 847, 623; HRMS (TOF ES): Found 252.1200, calculated for $\text{C}_{14}\text{H}_{16}\text{F}_2\text{NO}$ ($\text{M}+\text{H}$) 252.1200 (0.0 ppm).



1-(2-chloro-4-fluorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (53da)

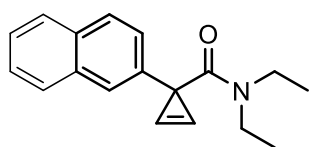
Compound was obtained via typical procedure A using 1-(2-chloro-4-fluorophenyl)cycloprop-2-ene-1-carboxylic acid (**50d**) (267 mg, 1.26 mmol, 1.0 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 83% yield (277 mg, 1.03 mmol). R_f : 0.27; mp: 81.1-82.6 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.28 (s, 2H), 7.25 – 7.19 (m, 1H), 6.98 (dd, J = 8.5, 2.6 Hz, 1H), 6.88 (ddd, J = 8.7, 7.8, 2.6 Hz, 1H), 3.25 (q, J = 7.1 Hz, 4H), 1.03 (t, J = 7.2 Hz, 3H), 0.62 (t, J = 7.1 Hz, 3H); ^{13}C (126 MHz, CDCl_3): δ 173.1, 161.2 (d, J = 249.5 Hz), 137.2 (d, J = 3.6 Hz), 134.4 (d, J = 10.1 Hz), 131.7 (+, d, J = 8.7 Hz), 117.2 (+, d, J = 24.3 Hz), 114.4 (+, d, J = 21.0 Hz), 110.1 (+, 2C), 41.8 (-), 40.2 (-), 31.5, 13.1 (+), 12.6 (+); FTIR (KBr, cm^{-1}): 3121, 3084, 2980, 2968, 2934, 1616, 1483, 1385, 1244, 1217, 1194, 1045, 889, 870, 652, 633; HRMS (TOF ES): Found 268.0905, calculated for $\text{C}_{14}\text{H}_{16}\text{ClFNO}$ ($\text{M}+\text{H}$) 268.0904 (0.2 ppm).



1-(2-bromo-4-fluorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (53ea)

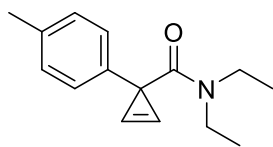
The titled compound was obtained via typical procedure using 1-(2-bromo-4-fluorophenyl)cycloprop-2-ene-1-carboxylic acid (**50e**) (263 mg, 1.02 mmol, 1.0 equiv.) as a colorless solid in 82% yield (262 mg, 0.84 mmol). R_f : 0.23; mp: 83.5 – 84.1 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.33 (s, 2H), 7.28 (dd, J = 8.6, 6.0 Hz, 1H), 7.22 (dd, J = 8.3, 2.6 Hz, 1H), 6.97 (ddd, J

= 8.7, 7.8, 2.6 Hz, 1H), 3.29 (q, J = 7.1 Hz, 4H), 1.07 (t, J = 7.1 Hz, 3H), 0.66 (t, J = 7.1 Hz, 3H); ^{13}C (126 MHz, CDCl_3): δ 173.1, 161.1 (d, J = 250.3 Hz), 138.8 (d, J = 3.6 Hz), 132.1 (+, d, J = 8.4 Hz), 123.4 (d, J = 9.5 Hz), 120.4 (+, d, J = 24.1 Hz), 115.0 (+, d, J = 21.0 Hz), 110.1 (+, 2C), 41.9 (-), 40.4 (-), 33.4, 13.1 (+), 12.6 (+); FTIR (KBr, cm^{-1}): 3122, 3082, 2979, 2966, 2943, 1643, 1614, 1579, 1479, 1384, 1259, 1238, 1191, 1099, 1070, 1037, 865, 649; HRMS (TOF ES): Found 334.0196, calculated for $\text{C}_{14}\text{H}_{15}\text{BrFNONa}$ ($\text{M}+\text{Na}$) 334.0219 (6.9 ppm).



N,N-diethyl-1-(naphthalen-2-yl)cycloprop-2-ene-1-carboxamide (53fa)

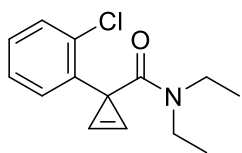
Compound was obtained via typical procedure A using 1-(naphthalen-2-yl)cycloprop-2-ene-1-carboxylic acid (**50f**) (85.0 mg, 0.404 mmol, 1.0 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 92% yield (98.0 mg, 0.370 mmol). R_f : 0.33; mp: 123.8-125.5 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3): δ 8.32 – 8.24 (m, 1H), 7.66 – 7.60 (m, 1H), 7.56 – 7.50 (m, 1H), 7.40 (s, 2H), 7.35 – 7.19 (m, 3H), 7.10 – 7.03 (m, 1H), 3.10 (q, J = 7.1 Hz, 2H), 3.04 (q, J = 7.1 Hz, 2H), 0.79 (t, J = 7.1 Hz, 3H), 0.13 (t, J = 7.0 Hz, 3H); ^{13}C (126 MHz, CDCl_3): δ 174.9, 141.0, 133.7, 132.7, 128.5 (+), 127.6 (+), 126.4 (+), 126.0 (+), 125.9 (+), 125.8 (+), 125.3 (+), 112.0 (+, 2C), 42.3 (+), 40.7 (+), 32.6, 13.0 (+), 12.8 (+); FTIR (KBr, cm^{-1}): 3074, 2974, 2931, 2872, 1614, 1454, 1427, 1271, 781, 667, 631; HRMS (TOF ES): Found 288.1364, calculated for $\text{C}_{18}\text{H}_{19}\text{NONa}$ ($\text{M}+\text{Na}$) 288.1364 (0.1 ppm).



N,N-diethyl-1-(p-tolyl)cycloprop-2-ene-1-carboxamide (53ga)

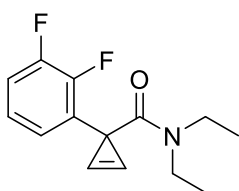
The titled compound was obtained via typical procedure using 1-(p-tolyl)cycloprop-2-ene-1-carboxylic acid (**50g**) (228 mg, 1.31 mmol, 1.0

equiv.) as a colorless solid in 86% yield (260 mg, 1.13 mmol). *R*_f: 0.26; mp: 80.5 – 81.7 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.24 (s, 2H), 7.12 – 7.07 (m, 2H), 7.04 – 6.99 (m, 2H), 3.39 (q, *J* = 7.1 Hz, 2H), 3.32 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 173.4, 140.6, 135.9, 129.1 (+, 2C), 125.9 (+, 2C), 109.9 (+, 2C), 41.9 (-), 39.0 (-), 31.8, 21.1 (+), 13.8 (+), 12.7 (+); FTIR (KBr, cm⁻¹): 3105, 3064, 2975, 2935, 2873, 1614, 1510, 1454, 1440, 1427, 1379, 1344, 1284, 1276, 1218, 1122, 1083, 1041, 810, 740; HRMS (TOF ES): Found 252.1373, calculated for C₁₅H₁₉NONa (M+Na) 252.1364 (3.6 ppm).



1-(2-chlorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide
(53ia)

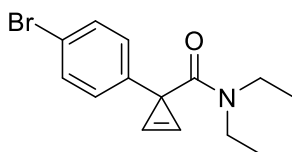
The titled compound was obtained via typical procedure using 1-(2-chlorophenyl)cycloprop-2-ene-1-carboxylic acid (**50i**) (237 mg, 1.22 mmol, 1.0 equiv.) as a very viscous colorless oil in 93% yield (285 mg, 1.14 mmol). *R*_f: 0.26; ¹H NMR (500 MHz, CDCl₃): δ 7.33 (s, 2H), 7.30 – 7.25 (m, 2H), 7.21 – 7.10 (m, 2H), 3.29 (q, *J* = 7.1 Hz, 4H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.61 (t, *J* = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 173.4, 141.1, 133.8, 130.7 (+), 130.2 (+), 128.1 (+), 127.1 (+), 110.1 (+, 2C), 41.9 (-), 40.2 (-), 32.2, 13.0 (+), 12.6 (+); FTIR (KBr, cm⁻¹): 3083, 2974, 2933, 2873, 1623, 1471, 1427, 1379, 1361, 1313, 1276, 1265, 1218, 1163, 1056, 1037, 748; HRMS (TOF ES): Found 272.0825, calculated for C₁₄H₁₆ClNONa (M+Na) 272.0818 (2.6 ppm).



1-(2,3-difluorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide
(53ja)

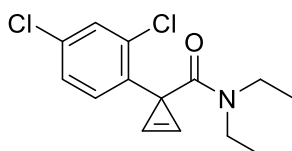
The titled compound was obtained via typical procedure using 1-(2,3-difluorophenyl)cycloprop-2-ene-1-carboxylic acid (**50j**) (264 mg, 1.35 mmol, 1.0 equiv.) as a colorless solid in 85% yield (289 mg, 1.15 mmol). *R*_f: 0.20; mp: 77.7 – 78.7 °C; ¹H NMR (500 MHz,

CDCl₃): δ 7.33 (s, 2H), 7.06 – 6.87 (m, 3H), 3.45 – 3.20 (m, 4H), 1.10 (t, J = 7.1 Hz, 3H), 0.79 (t, J = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 172.7, 150.8 (dd, J = 248.6, 13.0 Hz), 149.6 (dd, J = 248.9, 13.1 Hz), 133.4 (d, J = 9.1 Hz), 124.4 (+, t, J = 3.0 Hz), 124.1 (+, dd, J = 7.1, 4.7 Hz), 115.6 (+, d, J = 17.2 Hz), 110.2 (+, d, J = 2.1 Hz, 2C), 41.9 (-), 39.7 (-), 28.2 (d, J = 2.7 Hz), 13.4 (+), 12.6 (+); FTIR (KBr, cm⁻¹): 3080, 2975, 2935, 2875, 1625, 1589, 1479, 1442, 1427, 1380, 1272, 1253, 1218, 1041, 999, 873, 838, 784, 744; HRMS (TOF ES): Found 274.1021, calculated for C₁₄H₁₅F₂NONa (M+Na) 274.1019 (0.7 ppm).



1-(4-bromophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (53la)

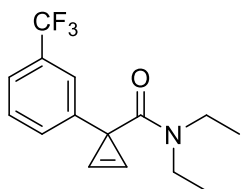
The titled compound was obtained via typical procedure using 1-(4-bromophenyl)cycloprop-2-ene-1-carboxylic acid (**50l**) (482 mg, 2.02 mmol, 1.0 equiv.) as a pale yellow solid in 89% yield (531 mg, 1.80 mmol). R_f : 0.23; mp: 92.9 – 94.4 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.46 – 7.32 (m, 2H), 7.23 (s, 2H), 7.03 – 6.94 (m, 2H), 3.38 (q, J = 7.1 Hz, 2H), 3.29 (q, J = 6.8 Hz, 2H), 1.15 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 172.7, 142.8, 131.5 (+, 2C), 127.8 (+, 2C), 120.2, 109.6 (+, 2C), 41.9 (-), 39.1 (-), 31.7, 13.9 (+), 12.7 (+); FTIR (KBr, cm⁻¹): 3078, 2974, 2933, 2873, 1623, 1485, 1460, 1429, 1380, 1313, 1282, 1218, 1118, 1072, 1006, 813; HRMS (TOF ES): Found 316.0317, calculated for C₁₄H₁₆BrNONa (M+Na) 316.0313 (1.3 ppm).



1-(2,4-dichlorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (53ma)

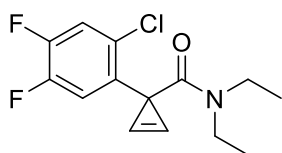
The titled compound was obtained via typical procedure using 1-(2,4-dichlorophenyl)cycloprop-2-ene-1-carboxylic acid (**50m**) (304 mg, 1.33 mmol, 1.0 equiv.) as a

colorless solid in 94% yield (356 mg, 1.25 mmol). *R*_f: 0.23; mp: 74.7 – 76.4 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.32 (s, 2H), 7.30 (d, *J* = 2.1 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.18 (dd, *J* = 8.3, 2.1 Hz, 1H), 3.29 (q, *J* = 7.1 Hz, 4H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.70 (t, *J* = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 172.9, 139.8, 134.5, 133.1, 131.6 (+), 129.9 (+), 127.5 (+), 110.0 (+, 2C), 41.9 (-), 40.3 (-), 31.7, 13.2 (+), 12.6 (+); FTIR (KBr, cm⁻¹): 3080, 2975, 2933, 2873, 1614, 1552, 1469, 1442, 1431, 1379, 1361, 1315, 1280, 1259, 1218, 1164, 1101, 1054, 852, 825, 794; HRMS (TOF ES): Found 306.0432, calculated for C₁₄H₁₅Cl₂NONa (M+Na) 306.0428 (1.3 ppm).



N,N-diethyl-1-(3-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxamide (53na)

The titled compound was obtained via typical procedure using 1-(3-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylic acid (**50n**) (443 mg, 1.94 mmol, 1.0 equiv.) as a colorless solid in 84% yield (461 mg, 1.63 mmol). *R*_f: 0.27; mp: 101.9 – 103.2 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.46 – 7.29 (m, 4H), 7.25 (s, 2H), 3.39 (q, *J* = 7.1 Hz, 2H), 3.29 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 172.4, 144.8, 130.8 (q, *J* = 32.1 Hz), 129.4 (+), 128.9 (+), 124.2 (q, *J* = 272.4 Hz), 123.2 (+, d, *J* = 3.8 Hz), 122.7 (+, d, *J* = 3.9 Hz), 109.3 (+, 2C), 41.9 (-), 39.0 (-), 31.9, 13.8 (+), 12.6 (+); FTIR (KBr, cm⁻¹): 3107, 3062, 2974, 2935, 2877, 1614, 1471, 1429, 1330, 1280, 1215, 1170, 1118, 1072, 1041, 906, 798, 694, 678; HRMS (TOF ES): Found 306.1080, calculated for C₁₅H₁₆F₃NONa (M+Na) 306.1082 (0.7 ppm).

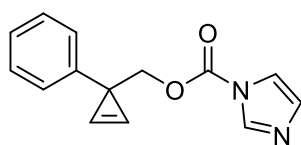


1-(2-chloro-4,5-difluorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (53oa)

The titled compound was obtained via typical procedure using 1-(2-chloro-4,5-difluorophenyl)cycloprop-2-ene-1-carboxylic acid (**50o**) (211 mg, 0.92 mmol, 1.0

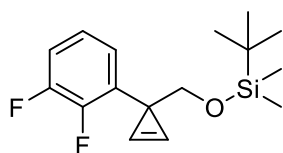
equiv.) as a colorless solid in 89% yield (233 mg, 0.815 mmol). *R*_f: 0.32; mp: 92.1 – 93.5 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.32 (s, 2H), 7.17 – 7.05 (m, 2H), 3.47 – 3.15 (m, 4H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 172.5, 149.2 (dd, *J* = 249.9, 12.6 Hz), 148.9 (dd, *J* = 251.9, 13.7 Hz), 138.2, 128.4 (dd, *J* = 7.7, 3.4 Hz), 119.0 (+, d, *J* = 20.0 Hz), 118.8 (+, d, *J* = 18.2 Hz), 110.1 (+, 2C), 41.9 (-), 40.3 (-), 31.7, 13.3 (+), 12.6 (+); FTIR (KBr, cm⁻¹): 3083, 2975, 2935, 2875, 1631, 1614, 1598, 1494, 1427, 1380, 1299, 1274, 1220, 1164, 1045, 1004, 900, 891, 790, 665; HRMS (TOF ES): Found 308.0635, calculated for C₁₄H₁₄ClF₂NONa (M+Na) 308.0630 (1.6 ppm).

2.12.3 Cyclopropenes Possessing Alternative Directing Groups



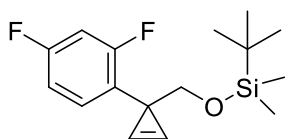
(1-phenylcycloprop-2-en-1-yl)methyl 1H-imidazole-1-carboxylate (43)

(1-phenylcycloprop-2-en-1-yl)methanol **(20a)** (250 mg, 1.71 mmol, 1.0 equiv.) was dissolved in dry tetrahydrofuran (17 mL) and cooled to 0 °C. Carbonyldiimidazole (305 mg, 1.88 mmol, 1.10 equiv.) was added and the reaction was allowed to warm to room temperature and stirred for 3 hours. Solvent was evaporated and the crude product was directly purified by silica gel column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained colorless solid in 97% yield (398.1 mg, 1.65 mmol). *R*_f: 0.57; ¹H NMR (500 MHz, CDCl₃) δ 8.13 – 8.04 (m, 1H), 7.40 – 7.36 (m, 1H), 7.34 – 7.28 (m, 4H), 7.24 – 7.18 (m, 3H), 7.06 – 7.01 (m, 1H), 4.84 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 148.7, 144.4, 137.1 (+), 130.6 (+), 128.4 (+, 2C), 126.3 (+), 126.1 (+, 2C), 117.1 (+), 111.8 (+, 2C), 75.1 (-), 25.9; FTIR (KBr, cm⁻¹): 3132, 3107, 3024, 2954, 1758, 1471, 1398, 1290, 1240, 1172, 1001, 752, 698; HRMS (TOF ES): Found 240.0898, calculated for C₁₄H₁₂N₂O₂ (M+) 240.0899 (0.4 ppm).



***tert*-butyl((1-(2,3-difluorophenyl)cycloprop-2-en-1-yl)methoxy)dimethylsilane (60)**

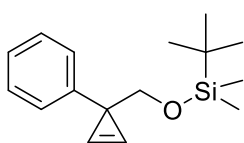
(1-(2,3-difluorophenyl)cycloprop-2-en-1-yl)methanol (**20j**) (290 mg, 1.59 mmol, 1.0 equiv.) was dissolved in dichloromethane (10 mL) and cooled to 0 °C. Triethylamine (670 µL, 4.78 mmol, 3.0 equiv.) and *tert*-butyldimethylsilyl chloride (360 mg, 2.39 mmol, 1.5 equiv.) were then added to the reaction mixture. The reaction was then allowed to warm to room temperature and stirred overnight. Saturated aqueous sodium bicarbonate was then added and stirred for one hour. Additional dichloromethane was added to the reaction and the product was extracted with dichloromethane (3 x 10 mL), dried, filtered, and concentrated. The product was then purified by silica gel column chromatography using a hexane:ethyl acetate (20:1) mobile phase. The titled compound was obtained as a clear oil in 92% yield (431 mg, 1.45 mmol). *R*_f: 0.15; ¹H NMR (500 MHz, CDCl₃): δ 7.49 (s, 2H), 7.06 – 6.91 (m, 3H), 3.87 (s, 2H), 0.84 (s, 9H), -0.04 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 150.8 (dd, *J* = 247.4, 13.4 Hz), 149.9 (dd, *J* = 246.5, 12.3 Hz), 135.6 (d, *J* = 12.7 Hz), 125.2 (+, t, *J* = 3.6 Hz), 123.8 (+, dd, *J* = 7.0, 4.6 Hz), 115.9 (+, 2C), 115.1 (+, d, *J* = 17.4 Hz), 69.0 (-, d, *J* = 2.2 Hz), 26.7, 26.0 (+, 3C), 18.5, -5.2 (+, 2C); ¹⁹F NMR (376 MHz, CDCl₃): δ -139.2 (d, *J* = 21.1 Hz), -143.5 (d, *J* = 21.2 Hz); FTIR (KBr, cm⁻¹): 2955, 2929, 2886, 2857, 1478, 1270, 1256, 1117, 1083, 837, 777, 728, 618; HRMS (TOF ES): Found 297.1502, calculated for C₁₆H₂₃F₂OSi (M+H) 297.1486 (5.4 ppm).



***tert*-butyl((1-(2,4-difluorophenyl)cycloprop-2-en-1-yl)methoxy)dimethylsilane (61)**

Procedure: (1-(2,4-difluorophenyl)cycloprop-2-en-1-yl)methanol (**20c**) (140 mg, 0.768 mmol, 1.0 equiv) was dissolved in dichloromethane (5 mL) and cooled to 0 °C. Triethylamine (323 µL, 2.31 mmol, 3.0 equiv.) and *tert*-butyldimethylsilyl chloride (174 mg,

1.15 mmol, 1.5 equiv.) were then added to the reaction mixture. The reaction was then allowed to warm to room temperature and was stirred overnight. Saturated aqueous sodium bicarbonate was then added and stirred for 1 hour. Additional dichloromethane was added to the reaction and the product was extracted with dichloromethane (3 x 10 mL), dried, filtered, and concentrated. The product was then purified by silica column chromatography using a hexane:ethyl acetate (20:1) mobile phase. The titled product was obtained as a clear oil in 90% yield (204 mg, 0.690 mmol). R_f : 0.16; ^1H NMR (500 MHz, CDCl_3): δ 7.54 (s, 2H), 7.20 (td, J = 8.5, 6.6 Hz, 1H), 6.86 – 6.71 (m, 2H), 3.87 (s, 2H), 0.88 (s, 9H), 0.00 (s, 6H); ^{13}C (126 MHz, CDCl_3): δ 161.7 (dd, J = 247.6, 11.7 Hz), 161.5 (dd, J = 245.4, 11.0 Hz), 131.3 (+, dd, J = 9.5, 7.0 Hz), 128.9 (dd, J = 16.3, 3.7 Hz), 116.1 (+, d, J = 1.8 Hz, 2C), 110.8 (+, dd, J = 20.7, 3.7 Hz), 103.6 (+, dd, J = 26.4, 25.0 Hz), 69.1 (-, d, J = 2.0 Hz), 26.2, 25.9 (+, 3C), 18.4, -5.3 (+, 2C); FTIR (KBr, cm^{-1}): 2954, 2929, 2885, 2856, 1641, 1614, 1596, 1502, 1463, 1421, 1269, 1255, 1135, 1091, 1047, 1004, 977, 964, 837, 775; HRMS (TOF ES): Found 319.1329, calculated for $\text{C}_{16}\text{H}_{22}\text{F}_2\text{O}_2\text{SiNa}$ ($\text{M}+\text{Na}$) 319.1306 (7.2 ppm).



***tert*-butyldimethyl((1-phenylcycloprop-2-en-1-yl)methoxy)silane**

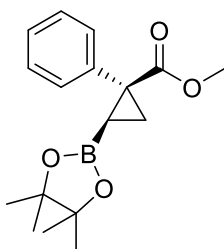
(62)

(1-phenylcycloprop-2-en-1-yl)methanol **(20a)** (250 mg, 1.71 mmol, 1.0

equiv.) was dissolved in dry dichloromethane and cooled to 0 °C. Triethylamine (716 μL , 5.13 mmol, 3.0 equiv.) was then added followed by *tert*-butyldimethylsilyl chloride (387 mg, 2.57 mmol, 1.5 equiv.). The reaction was allowed to warm to room temperature and then stir for 30 minutes. Excess saturated aqueous sodium bicarbonate was then added and the mixture was stirred for an additional 10 minutes. The reaction was then extracted with dichloromethane, dried, filtered, and concentrated. The product was purified by column chromatography using

20:1 hexane:ethyl acetate mobile phase. The titled product was obtained as pale yellow oil in 95% yield (422 mg, 1.62 mmol). *R*_f: 0.16; ¹H NMR (500 MHz, CDCl₃): δ 7.28 – 7.21 (m, 4H), 7.21 (s, 2H), 7.16 – 7.10 (m, 1H), 4.03 (s, 2H), 0.86 (s, 9H), -0.00 (s, 6H); ¹³C (126 MHz, CDCl₃): δ 129.3, 128.0 (+, 2C), 126.7 (+, 2C), 125.6 (+), 113.1 (+, 2C), 69.0 (-), 29.2, 26.1 (+, 3C), 18.6, -5.0 (+, 2C); FTIR (KBr, cm⁻¹): 3057, 3022, 2953, 2928, 2885, 2854, 1643, 1601, 1493, 1472, 1360, 1256, 1095, 1051, 1005, 972, 837, 775, 748, 696; HRMS (TOF ES): Found 260.1594, calculated for C₁₆H₂₄OSi (M⁺) 260.1596 (0.8 ppm).

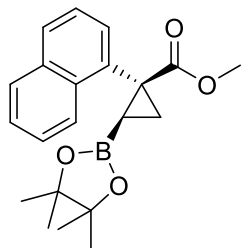
2.12.4 Directed Catalytic Asymmetric Hydroboration of Cyclopropene Esters



methyl 1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32a)

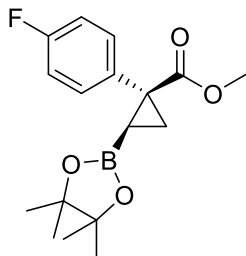
Typical Procedure (Direct Injection): A 1mL reaction vial was loaded with [Rh(COD)Cl]₂ (7.40 mg, 0.015 mmol, 0.03 equiv.) and (R)-BINAP (19.9 mg, 0.03 mmol, 0.06 equiv.) in a glove box. Freshly distilled and dried tetrahydrofuran (500 μL) was then added to the vial via syringe and the mixture was stirred until homogenous. Pinnacol borane (72.6 μL, 0.50 mmol, 1.0 equiv.) followed by methyl 1-phenylcycloprop-2-ene-1-carboxylate (**19a**) (87.1 mg, 0.50 mmol, 1.0 equiv.) were then added using a syringe. The reaction was then stirred for 30 minutes at room temperature. The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 99% yield (149 mg, 0.493 mmol). *R*_f: 0.52; dr: >99:1; er: 99:1; [α]_D²⁰ -57.89 (c = 4.067, CHCl₃); ¹H NMR (500 MHz, CDCl₃): 7.43 – 7.38 (m, 1H), 7.32 – 7.23 (m, 4H), 3.61 (s, 3H), 1.68 (dd, *J* = 8.4, 3.5 Hz, 1H), 1.35 (dd, *J* = 10.2, 3.5 Hz, 1H), 1.30 (s, 6H), 1.29 (s, 6H), 0.76 (dd, *J* = 10.2, 8.4 Hz, 1H); ¹³C (126 MHz, CDCl₃): δ 174.5, 140.4, 130.3 (+, 2C), 128.2 (+, 2C), 127.3 (+),

83.7 (2C), 52.5 (+), 34.5, 25.1 (+, 4C), 19.1 (-), 11.9; ^{19}F NMR (376 MHz, CDCl_3) δ -115.2 (s, 1F); FTIR (KBr, cm^{-1}): 3052, 3026, 2978, 2949, 2932, 1718, 1435, 1410, 1391, 1371, 1313, 1292, 1215, 1198, 1167, 1144, 1107, 972, 858, 768, 752, 700, 667; HRMS (TOF ES): Found 302.1685, calculated for $\text{C}_{17}\text{H}_{23}\text{BO}_4$ (M^+) 302.1689 (1.3 ppm).



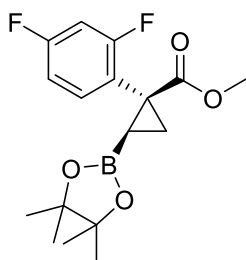
methyl 1-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32f)

Typical Procedure (Dissolved Method): A 1mL reaction vial was loaded with $[\text{Rh}(\text{COD})\text{Cl}]_2$ (3.75 mg, 7.50 μmol , 0.03 equiv.) and (R)-BINAP (10.0 mg, 0.015 mmol, 0.06 equiv.) in a glove box. Freshly distilled and dried tetrahydrofuran (500 μL) was then added to the vial via syringe and the mixture was stirred until homogenous. Pinnacol borane (37.0 μL , 0.25 mmol, 1.0 equiv.) followed by methyl 1-(naphthalen-1-yl)cycloprop-2-ene-1-carboxylate (**19f**) (56.1 mg, 0.25 mmol, 1.0 equiv.) dissolved in a minimal amount of tetrahydrofuran were then added using a syringe. The reaction was then stirred for 30 minutes at room temperature. The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 99% yield (87.2 mg, 0.248 mmol). R_f : 0.52; dr: 97:3; er: 96.5:3.5; $[\alpha]_{\text{D}}^{20}$ -40.63 (c = 2.267, CHCl_3); mp: 122.3 – 124.7 $^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3): δ 8.29 (d, J = 8.4 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.81 – 7.75 (m, 1H), 7.60 – 7.44 (m, 3H), 7.45 – 7.37 (m, 1H), 3.53 (s, 3H), 1.98 – 1.85 (m, 1H), 1.54 – 1.43 (m, 1H), 1.35 (s, 6H), 1.34 (s, 6H), 0.95 – 0.80 (m, 1H); ^{13}C (126 MHz, CDCl_3): δ 174.9, 136.9, 133.7, 133.3, 128.6 (+), 128.2 (+), 127.9 (+), 126.4 (+), 125.7 (+), 125.3 (+), 125.1 (+), 83.8 (2C), 52.6 (+), 32.1, 25.2 (+, 2C), 25.1 (+, 2C), 20.2 (-), 13.4; FTIR (KBr, cm^{-1}): 3045, 2976, 2949, 2930, 1717, 1437, 1414, 1391, 1312, 1288, 1223, 1202, 1165, 1144, 970, 858, 800, 779, 736, 685; HRMS (TOF ES): Found 352.1844, calculated for $\text{C}_{21}\text{H}_{25}\text{BO}_4$ (M^+) 352.1846 (0.6 ppm).



methyl 1-(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32b)

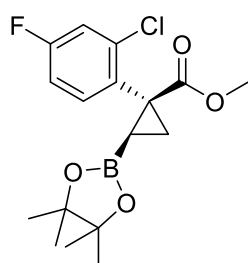
Compound was obtained via typical procedure for direct injection using methyl 1-(4-fluorophenyl)cycloprop-2-ene-1-carboxylate (**19b**) (48.0 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 80% yield (63.8 mg, 0.20 mmol). R_f : 0.52; dr: 98:2; er: 96:4; $[\alpha]_D^{20}$ -40.56 (c = 0.900, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.38 – 7.33 (m, 2H), 6.99 – 6.93 (m, 2H), 3.61 (s, 3H), 1.67 (dd, J = 8.4, 3.5 Hz, 1H), 1.32 (dd, J = 10.7, 3.9 Hz, 1H), 1.30 (s, 6H), 1.28 (s, 6H), 0.71 (dd, J = 10.2, 8.4 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 174.3, 162.0 (d, J = 245.7 Hz), 136.2 (d, J = 3.2 Hz), 132.0 (+, d, J = 8.1 Hz, 2C), 115.0 (+, d, J = 21.4 Hz, 2C), 83.7 (2C), 52.6 (+), 33.7, 25.1 (+, 4C), 19.2 (-), 12.1; ^{19}F NMR (376 MHz, CDCl_3) δ -115.2 (s, 1F); FTIR (KBr, cm^{-1}): 3050, 2978, 2951, 2932, 1724, 1605, 1514, 1437, 1414, 1371, 1315, 1292, 1273, 1221, 1200, 1167, 1144, 1105, 972, 858, 837, 814, 775, 684; HRMS (TOF ES): Found 321.1669, calculated for $\text{C}_{17}\text{H}_{23}\text{BF}_4\text{O}_4$ ($\text{M}+\text{H}$) 321.1673 (1.2 ppm).



methyl 1-(2,4-difluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32c)

Compound was obtained via typical procedure for dissolved method using methyl 1-(2,4-difluorophenyl)cycloprop-2-ene-1-carboxylate (**19c**) (52.5 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 60% yield (50.2 mg, 0.150 mmol). R_f : 0.54; dr: 57:43; er: 90:10 (major), 68:32 (minor); $[\alpha]_D^{20}$ -48.46 (c = 0.867, CHCl_3); ^1H NMR (500 MHz, CDCl_3): [7.36 – 7.17 (m), Σ 1H], [6.85 – 6.67 (m), Σ 2H], [3.60

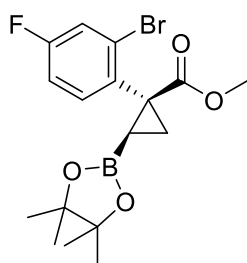
(s) & 3.60 (s, $\Sigma 3H$), [1.78 – 1.71 (m), $\Sigma 1H$], [1.49 (dd, $J = 8.23, 3.43$ Hz) & 0.74 (dd, $J = 10.39, 8.77$ Hz), $\Sigma 1H$], [1.37 – 1.25 (m) & 1.08 (s) & 0.93 (s), $\Sigma 13H$]; ^{13}C (126 MHz, $CDCl_3$): δ [173.7 (s), $\Sigma 1C$], [164.0 – 160.9 (m), $\Sigma 2C$], [132.8 (+, dd, $J = 9.72, 5.34$ Hz) & 132.3 (+, dd, $J = 9.69, 5.10$ Hz), $\Sigma 1C$], [123.8 (dd, $J = 14.84, 3.80$ Hz) & 121.9 (dd, $J = 14.69, 3.85$ Hz), $\Sigma 1C$], [111.4 – 108.9 (+, m), $\Sigma 1C$], [105.3 – 102.3 (+, m), $\Sigma 1C$], [83.7 (s) & 83.4 (s), $\Sigma 2C$], [52.6 (+, s) & 52.5 (+, s), $\Sigma 1C$], [28.4 (s) & 27.9 (s), $\Sigma 1C$], [25.0 (+, s) & 24.7 (+, s), $\Sigma 2C$], [24.9 (+, s) & 24.4 (+, s), $\Sigma 2C$], [19.3 (-, s), $\Sigma 1C$], [12.5 (s), $\Sigma 1C$]; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.6 (d, $J = 8.0$ Hz, 1F), -111.6 (d, $J = 8.0$ Hz, 1F); FTIR (KBr, cm^{-1}): 3068, 2980, 2932, 1728, 1616, 1508, 1437, 1410, 1333, 1269, 1213, 1167, 1142, 1111, 968, 856, 698, 669; HRMS (TOF ES): Found 338.1498, calculated for $C_{17}H_{21}BF_2O_4$ (M⁺) 338.1501 (0.9 ppm).



methyl 1-(2-chloro-4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32d)

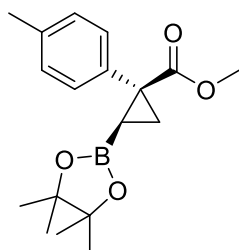
Compound was obtained via typical procedure for dissolved method using methyl 1-(2-chloro-4-fluorophenyl)cycloprop-2-ene-1-carboxylate (**19d**) (56.7 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 92% yield (81.6 mg, 0.230 mmol). R_f : 0.54; dr: 94:6; er: 83:17; $[\alpha]_D^{20}$ -47.75 ($c = 2.367$, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, $J = 8.6, 6.0$ Hz, 1H), 7.10 (dd, $J = 8.5, 2.7$ Hz, 1H), 6.91 (td, $J = 8.3, 2.6$ Hz, 1H), 3.60 (s, 3H), 1.83 (dd, $J = 8.8, 3.8$ Hz, 1H), 1.30 (s, 6H), 1.31 – 1.27 (m, 1H), 1.28 (s, 6H), 0.79 (dd, $J = 10.4, 8.8$ Hz, 1H); ^{13}C (126 MHz, $CDCl_3$): δ 173.7, 161.8 (d, $J = 249.3$ Hz), 137.5 (d, $J = 10.5$ Hz), 134.6 (d, $J = 3.6$ Hz), 132.9 (+, d, $J = 8.8$ Hz), 116.8 (+, d, $J = 24.8$ Hz), 113.6 (+, d, $J = 21.0$ Hz), 83.8 (2C), 52.6 (+), 32.0, 25.1(+, 2C), 25.0 (+, 2C), 20.5 (-), 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.1 (s, 1F); FTIR (KBr, cm^{-1}): 3071, 2978, 2951, 2932, 1726, 1602, 1495, 1437, 1410, 1317,

1290, 1261, 1219, 1202, 1169, 1144, 1109, 972, 905, 858, 829, 684; HRMS (TOF ES): Found 355.1288, calculated for $C_{17}H_{22}BClFO_4$ ($M+H$) 355.1284 (1.1 ppm).



methyl 1-(2-bromo-4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32e)

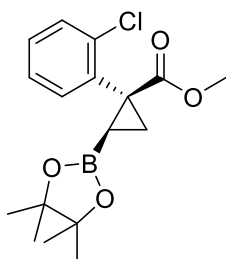
Compound was obtained via typical procedure for dissolved method using methyl 1-(2-bromo-4-fluorophenyl)cycloprop-2-ene-1-carboxylate (**19e**) (67.8 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 81% yield (80.9 mg, 0.208 mmol). R_f : 0.50; dr: 97:3; er: 93.5:6.5; $[\alpha]_D^{20}$ -38.22 ($c = 1.667$, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, $J = 8.6, 5.9$ Hz, 1H), 7.29 (dd, $J = 8.2, 2.6$ Hz, 1H), 6.96 (td, $J = 8.3, 2.7$ Hz, 1H), 3.61 (s, 3H), 1.87 (dd, $J = 8.8, 3.8$ Hz, 1H), 1.30 (s, 6H), 1.31 – 1.28 (m, 1H), 1.28 (s, 6H), 0.82 (dd, $J = 10.5, 8.8$ Hz, 1H); ^{13}C (126 MHz, $CDCl_3$): δ 173.6, 161.6 (d, $J = 250.3$ Hz), 136.2 (d, $J = 3.5$ Hz), 133.1 (+, d, $J = 8.5$ Hz), 127.3 (d, $J = 9.6$ Hz), 120.0 (+, d, $J = 24.4$ Hz), 114.2 (+, d, $J = 20.9$ Hz), 83.8 (2C), 52.6 (+), 34.0, 25.1 (+, 2C), 25.0 (+, 2C), 21.2 (-), 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2 (s, 1F); FTIR (KBr, cm^{-1}): 3067, 2978, 2951, 2932, 1726, 1597, 1583, 1489, 1437, 1410, 1371, 1315, 1290, 1263, 1217, 1202, 1169, 1144, 1109, 972, 883, 856, 829; HRMS (TOF ES): Found 398.0703, calculated for $C_{17}H_{21}BBrFO_4$ ($M+$) 398.0700 (0.8 ppm).



methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)cyclopropanecarboxylate (32g)

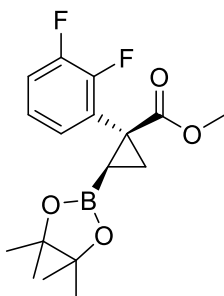
Compound was obtained via typical procedure for direct injection using methyl 1-(p-tolyl)cycloprop-2-ene-1-carboxylate (**19g**) (47.1 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl

acetate mobile phase. The titled compound was obtained as a pale yellow oil in 94% yield (73.8 mg, 0.233 mmol). R_f : 0.52; dr: >99:1; er: 97.5:2.5; $[\alpha]_D^{20}$ -62.39 (c = 2.300, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.33 – 7.27 (m, 2H), 7.12 – 7.07 (m, 2H), 3.61 (s, 3H), 2.33 (s, 3H), 1.65 (dd, J = 8.4, 3.5 Hz, 1H), 1.32 (dd, J = 10.2, 3.4 Hz, 1H), 1.30 (s, 6H), 1.29 (s, 6H), 0.73 (dd, J = 10.2, 8.4 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 174.6, 137.5, 137.0, 130.2 (+, 2C), 128.9 (+, 2C), 83.6 (2C), 52.5 (+), 34.1, 25.1 (+, 4C), 21.3, 19.2 (-), 12.0; FTIR (KBr, cm^{-1}): 2978, 2949, 2928, 2872, 1718, 1516, 1437, 1412, 1371, 1313, 1290, 1273, 1213, 1198, 1167, 1144, 1105, 1049, 972, 858, 824, 773, 685; HRMS (TOF ES): Found 316.1837, calculated for $\text{C}_{18}\text{H}_{25}\text{BO}_4$ (M^+) 316.1846 (2.8 ppm).



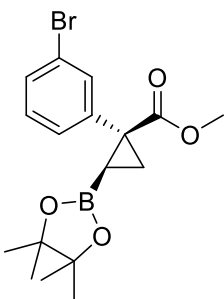
methyl 1-(2-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32i)

Compound was obtained via typical procedure for dissolved method using methyl 1-(2-chlorophenyl)cycloprop-2-ene-1-carboxylate (**19i**) (52.2 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 91% yield (76.6 mg, 0.228 mmol). R_f : 0.52; dr: 89:11; er: 97:3; $[\alpha]_D^{20}$ -53.50 (c = 1.200, CHCl_3); mp: 83.6 – 84.4 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.41 – 7.32 (m, 2H), 7.22 – 7.18 (m, 2H), 3.60 (s, 3H), 1.84 (dd, J = 8.8, 3.8 Hz, 1H), 1.33 – 1.29 (m, 1H), 1.31 (s, 6H), 1.29 (s, 6H), 0.83 (dd, J = 10.4, 8.8 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 173.9, 138.5, 136.8, 131.8 (+), 129.4 (+), 128.6 (+), 126.5 (+), 83.7 (2C), 52.6 (+), 32.7, 25.1 (+, 2C), 25.0 (+, 2C), 20.4 (-), 13.6; FTIR (KBr, cm^{-1}): 3070, 2978, 2949, 2932, 1724, 1437, 1408, 1315, 1290, 1296, 1215, 1200, 1169, 1144, 1111, 1068, 1041, 972, 858, 754; HRMS (TOF ES): Found 336.1309, calculated for $\text{C}_{17}\text{H}_{22}\text{BClO}_4$ (M^+) 336.1300 (2.7 ppm).



methyl 1-(2,3-difluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32j)

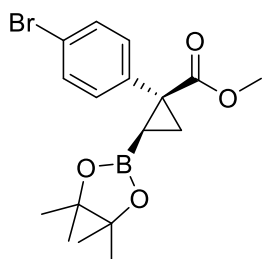
Compound was obtained via typical procedure for direct injection using methyl 1-(2,3-difluorophenyl)cycloprop-2-ene-1-carboxylate (**19j**) (52.5 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless oil in 55% yield (46.1 mg, 0.138 mmol). *R_f*: 0.54; dr:54:46; er: 90:10 (major), 88:12 (minor); [α]_D²⁰ -49.17 (*c* = 0.767, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ [7.12 – 6.95 (m), Σ 3H], [3.69 & 3.62 (s), Σ 3H], [1.80 – 1.73 (m), Σ 1H], [1.54 – 1.48 (m) & 0.84 – 0.73 (m), Σ 1H], [1.38 – 1.32 (m), Σ 1H], [1.31 (s) & 1.08 (s), Σ 6H], [1.29 (s) & 0.93 (s), Σ 6H]; ¹³C (126 MHz, CDCl₃): δ [173.5 (s) & 173.5 (s), Σ 1C], [152.0 – 151.3 (m) & 150.0 – 149.2 (m), Σ 2C], [130.2 (d, *J* = 9.82 Hz) & 128.3 (d, *J* = 11.30 Hz) & 127.0 (+, s) & 126.3 (+, s) & 124.5 – 122.7 (+, m) & 117.5 – 115.6 (+, m) & 107.8 (s), Σ 4C], [83.8 (s) & 83.5 (s), Σ 2C], [52.8 (+, s) & 52.7 (+, s), Σ 1C], [28.8 (s) & 28.3 (s), Σ 1C], [25.1 (+, s) & 24.8 (+, s), Σ 2C], [25.0 (+, s) & 24.5 (+, s), Σ 2C], [19.6 (-, s) & 19.4 (-, s), Σ 1C], [12.6 (s), Σ 1C]; ¹⁹F NMR (376 MHz, CDCl₃) δ -138.1 (d, *J* = 21.0 Hz, 1F), -139.8 (d, *J* = 20.8 Hz, 1F); FTIR (KBr, cm⁻¹): 2980, 2953, 2932, 1730, 1481, 1448, 1437, 1412, 1335, 1267, 1227, 1198, 1163, 1142, 968, 858, 787, 742, 719; HRMS (TOF ES): Found 345.1648, calculated for C₁₇H₂₁BF₂O₄Li (M+Li) 345.1661 (3.8 ppm).



methyl 1-(3-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32k)

Compound was obtained via typical procedure for dissolved method using methyl 1-(3-bromophenyl)cycloprop-2-ene-1-carboxylate (**19k**) (63.3 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column

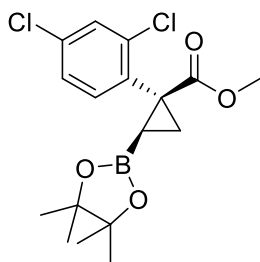
chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 90% yield (85.9 mg, 0.225 mmol). *R_f*: 0.53; dr: 85:15; er: 99:1; [α]_D²⁰ -35.54 (*c* = 1.300, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.56 – 7.53 (m, 1H), 7.39 – 7.35 (m, 1H), 7.34 – 7.31 (m, 1H), 7.18 – 7.13 (m, 1H), 3.61 (s, 3H), 1.67 (dd, *J* = 8.5, 3.6 Hz, 1H), 1.34 (dd, *J* = 10.3, 3.6 Hz, 1H), 1.30 (s, 6H), 1.29 (s, 6H), 0.74 (dd, *J* = 10.3, 8.5 Hz, 1H); ¹³C (126 MHz, CDCl₃): δ 173.9, 142.6, 133.4 (+), 130.5 (+), 129.7 (+), 129.1 (+), 122.1, 83.8 (2C), 52.7 (+), 34.0, 25.1 (+, 2C), 25.1 (+, 2C), 19.2 (-), 12.3; FTIR (KBr, cm⁻¹): 3109, 3061, 2978, 2951, 2932, 1724, 1595, 1564, 1477, 1437, 1408, 1315, 1288, 1215, 1200, 1167, 1144, 1111, 972, 883, 858, 779, 696; HRMS (TOF ES): Found 381.0881, calculated for C₁₇H₂₃BBrO₄ (M+H) 381.0873 (2.1 ppm).



methyl 1-(4-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32l)

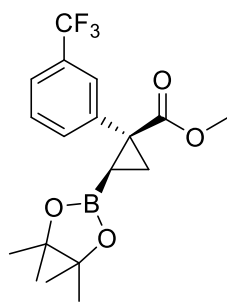
Compound was obtained via typical procedure for dissolved method using methyl 1-(4-bromophenyl)cycloprop-2-ene-1-carboxylate (**19l**)

(63.3 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 89% yield (84.6 mg, 0.222 mmol). *R_f*: 0.53; dr: 98:2; er: 96.5:3.5; [α]_D²⁰ -51.86 (*c* = 1.167, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.45 – 7.40 (m, 2H), 7.31 – 7.26 (m, 2H), 3.63 (s, 3H), 1.69 (dd, *J* = 8.5, 3.6 Hz, 1H), 1.35 – 1.32 (m, 1H), 1.32 (s, 6H), 1.30 (s, 6H), 0.73 (dd, *J* = 10.3, 8.5 Hz, 1H); ¹³C (126 MHz, CDCl₃): δ 174.0, 139.5, 132.1 (+, 2C), 131.3 (+, 2C), 121.3, 83.8 (2C), 52.6 (+), 33.8, 25.0 (+, 4C), 19.2 (-), 12.2; FTIR (KBr, cm⁻¹): 2978, 2932, 1722, 1489, 1435, 1410, 1313, 1288, 1215, 1198, 1167, 1144, 1101, 1011, 972, 858, 827; HRMS (TOF ES): Found 381.0884, calculated for C₁₇H₂₃BBrO₄ (M+H) 381.0873 (2.9 ppm).



methyl 1-(2,4-dichlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32m)

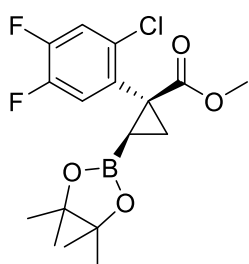
Compound was obtained via typical procedure for dissolved method using methyl 1-(2,4-dichlorophenyl)cycloprop-2-ene-1-carboxylate (**19m**) (60.8 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 83% yield (76.3 mg, 0.206 mmol). R_f : 0.53; dr: 84:16; er:83:17; $[\alpha]_D^{20}$ -54.49 (c = 1.633, CHCl_3); mp: 129.2 – 130.9 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.38 – 7.35 (m, 1H), 7.32 – 7.28 (m, 1H), 7.23 – 7.16 (m, 1H), 3.60 (s, 3H), 1.83 (dd, J = 8.8, 3.8 Hz, 1H), 1.30 (s, 6H), 1.31 – 1.28 (m, 1H), 1.28 (s, 6H), 0.79 (dd, J = 10.5, 8.8 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 173.5, 137.5, 137.2, 133.8, 132.7 (+), 129.3 (+), 126.8 (+), 83.8 (2C), 52.7 (+), 32.1, 25.1 (+, 2C), 25.0 (+, 2C), 20.5 (-), 13.8; FTIR (KBr, cm^{-1}): 2978, 2951, 2930, 1726, 1479, 1437, 1410, 1379, 1315, 1288, 1215, 1200, 1169, 1144, 1103, 970, 858, 827, 806; HRMS (TOF ES): Found 371.0992, calculated for $\text{C}_{17}\text{H}_{22}\text{BCl}_2\text{O}_4$ ($\text{M}+\text{H}$) 371.0988 (1.1 ppm).



methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3-(trifluoromethyl)phenyl)cyclopropanecarboxylate (32n)

Compound was obtained via typical procedure for dissolved method using methyl 1-(3-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylate (**19n**) (60.5 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 75% yield (68.6 mg, 0.185 mmol). R_f : 0.53; dr: 96:4; er: 96:4; $[\alpha]_D^{20}$ -39.08 (c = 1.333, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.66 – 7.61 (m, 1H), 7.61 – 7.57 (m, 1H), 7.53 – 7.47 (m, 1H), 7.44 – 7.37 (m, 1H), 3.62 (s, 3H), 1.73 (dd, J = 8.5, 3.6 Hz, 1H), 1.36 (dd, J = 10.4, 3.6

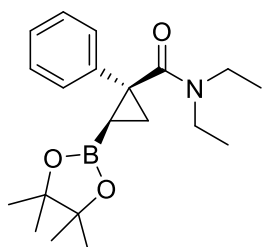
Hz, 1H), 1.31 (s, 6H), 1.29 (s, 6H), 0.77 (dd, $J = 10.3, 8.5$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 173.8, 141.3, 134.0 (+), 130.5 (q, $J = 32.1$ Hz), 128.6 (+), 127.0 (+, d, $J = 3.8$ Hz), 124.2 (+, d, $J = 3.9$ Hz), 124.2 (q, $J = 272.3$ Hz), 83.8 (2C), 52.7 (+), 34.1, 25.1 (+, 4C), 19.2 (-), 12.3; ^{19}F NMR (376 MHz, CDCl_3) δ -62.4 (s, 3F); FTIR (KBr, cm^{-1}): 3065, 2980, 2953, 2934, 1726, 1437, 1410, 1371, 1340, 1319, 1308, 1275, 1215, 1200, 1165, 1144, 1128, 1097, 1074, 1057, 972, 858, 800, 704; HRMS (TOF ES): Found 370.1559, calculated for $\text{C}_{18}\text{H}_{22}\text{BF}_3\text{O}_4$ (M^+) 370.1563 (1.1 ppm).



methyl 1-(2-chloro-4,5-difluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (32o)

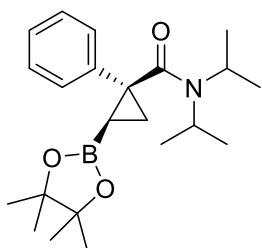
Compound was obtained via typical procedure for dissolved method using methyl 1-(2-chloro-4,5-difluorophenyl)cycloprop-2-ene-1-carboxylate (**19o**) (61.2 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 83% yield (77.4 mg, 0.208 mmol). R_f : 0.50; dr: 75:25; er: 93:7; $[\alpha]_D^{20}$ -38.65 ($c = 1.433$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.24 – 7.12 (m, 2H), 3.61 (s, 3H), 1.84 (dd, $J = 8.8, 3.9$ Hz, 1H), 1.30 (s, 6H), 1.31 – 1.28 (m, 1H), 1.28 (s, 6H), 0.77 (dd, $J = 10.5, 8.8$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 173.1, 149.4 (dd, $J = 251.7, 13.5$ Hz), 148.6 (dd, $J = 248.8, 12.5$ Hz), 135.4 (dd, $J = 5.7, 3.9$ Hz), 131.5 (dd, $J = 7.9, 3.6$ Hz), 120.4 (+, d, $J = 18.6$ Hz), 118.4 (+, d, $J = 20.3$ Hz), 83.9 (2C), 52.7 (+), 32.1, 25.1 (+, 2C), 25.0 (+, 2C), 20.6 (-), 14.0; ^{19}F NMR (376 MHz, CDCl_3) δ -136.7 (d, $J = 21.2$ Hz, 1F), -139.5 (d, $J = 21.2$ Hz, 1F); FTIR (KBr, cm^{-1}): 3117, 3055, 2980, 2953, 1730, 1603, 1499, 1437, 1412, 1391, 1321, 1298, 1271, 1250, 1182, 1163, 1144, 1107, 970, 858, 800, 775; HRMS (TOF ES): Found 372.1127, calculated for $\text{C}_{17}\text{H}_{20}\text{BClF}_2\text{O}_4$ (M^+) 372.1111 (4.3 ppm).

2.12.5 Directed Catalytic Asymmetric Hydroboration of Cyclopropene Amides



(1*S*,2*R*)-N,N-diethyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54aa)

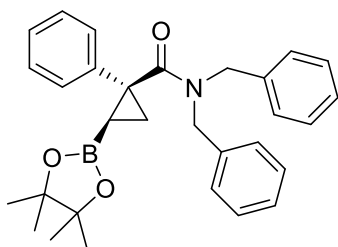
Compound was obtained via typical procedure for dissolved method using N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (53.8 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 92% yield (78.5 mg, 0.229 mmol). R_f : 0.37; dr: >98:2; er: 96:4; $[\alpha]_D^{20}$ 43.24 ($c = 1.133$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.33 – 7.23 (m, 4H), 7.21 – 7.13 (m, 1H), 3.50 – 3.29 (m, 2H), 3.27 – 3.14 (m, 2H), 1.65 (dd, $J = 9.8, 3.9$ Hz, 1H), 1.41 (dd, $J = 7.5, 3.9$ Hz, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.16 (t, $J = 7.1$ Hz, 3H), 0.71 (t, $J = 7.1$ Hz, 3H), 0.65 (dd, $J = 9.8, 7.5$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 175.5, 140.1, 128.7 (+, 2C), 127.7 (+, 2C), 126.8 (+), 81.4 (2C), 43.1 (-), 42.1 (-), 36.0, 25.2 (+, 2C), 25.1 (+, 2C), 19.5 (-), 18.7, 12.6 (+), 12.6 (+); FTIR (KBr, cm^{-1}): 3061, 2976, 2935, 2876, 1643, 1634, 1601, 1470, 1454, 1404, 1381, 1325, 1211, 1142, 1115, 953, 860, 760, 700; HRMS (TOF ES): Found 366.2214, calculated for $\text{C}_{20}\text{H}_{30}\text{BNO}_3\text{Na}$ ($\text{M}+\text{Na}$) 366.2216 (0.5 ppm).



(1*S*,2*R*)-N,N-diisopropyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ab)

Compound was obtained via typical procedure for dissolved method using N,N-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ab**) (60.8 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound

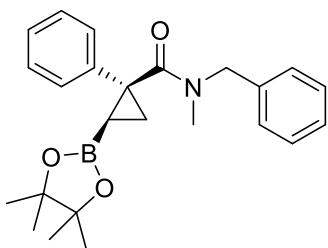
was obtained as a pale yellow oil in 83% yield (77.2 mg, 0.208 mmol). R_f : 0.30; dr: >98:2; er: 83:17; $[\alpha]_D^{20}$ 52.50 ($c = 1.333$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.25 – 7.22 (m, 4H), 7.18 – 7.13 (m, 1H), 4.27 – 4.14 (m, 1H), 3.41 – 3.28 (m, 1H), 1.74 (dd, $J = 9.9, 4.0$ Hz, 1H), 1.43 (d, $J = 6.9$ Hz, 3H), 1.42 (d, $J = 6.8$ Hz, 3H), 1.33 (dd, $J = 7.5, 4.0$ Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.03 (d, $J = 6.7$ Hz, 3H), 0.58 (d, $J = 6.6$ Hz, 3H), 0.50 (dd, $J = 9.8, 7.5$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 176.1, 140.3, 128.7 (+, 2C), 127.5 (+, 2C), 126.6 (+), 80.9 (2C), 50.9 (+), 47.3 (+), 37.3, 25.3 (+, 2C), 25.2 (+, 2C), 21.0 (+), 20.7 (+), 20.0 (+), 19.8, 18.5 (+), 18.4 (-); FTIR (KBr, cm^{-1}): 2972, 2932, 1634, 1591, 1470, 1441, 1404, 1371, 1346, 1290, 1265, 1209, 1146, 1115, 1036, 964, 862, 760, 700; HRMS (TOF ES): Found 394.2522, calculated for $\text{C}_{22}\text{H}_{34}\text{BNO}_3\text{Na}$ ($\text{M}+\text{Na}$) 394.2529 (1.8 ppm).



(1S,2R)-N,N-dibenzyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ad)

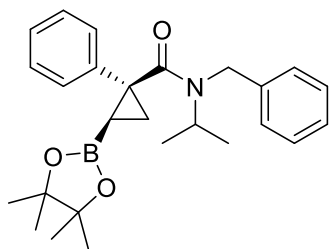
Compound was obtained via typical procedure for dissolved method using N,N-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ad**) (85.0 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 98% yield (115 mg, 0.246 mmol). R_f : 0.48; dr: >98:2; er: 96.5:3.5; $[\alpha]_D^{20}$ 9.67 ($c = 0.900$, CHCl_3); mp: 115.9 – 117.6 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.38 – 7.14 (m, 13H), 6.87 – 6.77 (m, 2H), 4.46 (s, 4H), 1.75 (dd, $J = 9.7, 4.1$ Hz, 1H), 1.59 (dd, $J = 7.7, 4.2$ Hz, 1H), 1.34 (s, 6H), 1.29 (s, 6H), 0.61 (dd, $J = 9.7, 7.7$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 173.4, 140.6, 136.9, 135.8, 128.8 (+, 2C), 128.7 (+, 2C), 128.6 (+, 2C), 128.6 (+, 2C), 127.8 (+, 2C), 127.6 (+), 127.5 (+), 127.1 (+, 2C), 126.9 (+), 82.9 (2C), 50.2 (-), 47.6 (-), 36.9, 25.2 (+, 2C), 25.1 (+, 2C), 18.0 (-), 15.6; FTIR (KBr, cm^{-1}): 3060, 3028, 2976, 2928, 1939, 1601, 1495, 1421,

1404, 1325, 1290, 1267, 1209, 1192, 1144, 1007, 962, 862, 737, 700; HRMS (TOF ES): Found 490.2530, calculated for $C_{30}H_{34}BNO_3Na$ ($M+Na$) 490.2529 (0.2 ppm).



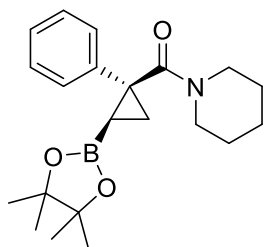
(1S,2R)-N-benzyl-N-methyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ae)

Compound was obtained via typical procedure for dissolved method using N-benzyl-N-methyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ae**) (66.0 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 73% yield (71.1 mg, 0.182 mmol). R_f : 0.38; dr: >98:2; er: 93.5:6.5; $[\alpha]_D^{20}$ -8.78 ($c = 1.833$, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$): δ [7.38 – 7.12 (m), $\Sigma 10H$], [4.98 (d, $J = 14.5$ Hz) & 4.85 (d, $J = 15.5$ Hz), $\Sigma 1H$], [4.20 (d, $J = 14.6$ Hz) & 4.14 (d, $J = 15.5$ Hz), $\Sigma 1H$], [2.83 (s) & 2.75 (s), $\Sigma 3H$], [1.68 – 1.52 (m), $\Sigma 2H$], [1.31 (s) & 1.29 (s), $\Sigma 6H$], [1.27 (s) & 1.25 (s), $\Sigma 6H$], [0.78 – 0.68 (m), $\Sigma 1H$]; ^{13}C (126 MHz, $CDCl_3$): δ [173.0 & 174.6, $\Sigma 1C$], [140.3 & 140.2, $\Sigma 1C$], [136.9 & 135.6, $\Sigma 1C$], [128.7 & 128.6 & 128.5 & 128.3 & 127.6 & 127.4 & 127.4 & 127.3 & 126.5 & 126.5 & 126.2, (+), $\Sigma 10C$], [82.8 & 82.3, $\Sigma 2C$], [51.9 & 53.8, (-), $\Sigma 1C$], [36.3 & 36.2, $\Sigma 1C$], [35.4 & 34.1, (+), $\Sigma 1C$], [25.1 & 25.2, (+), $\Sigma 2C$], [24.8 & 24.9, (+), $\Sigma 2C$], 19.3 (-), 15.2; FTIR (KBr, cm^{-1}): 3058, 3026, 2974, 2925, 1641, 1602, 1496, 1481, 1444, 1429, 1400, 1325, 1290, 1269, 1211, 1143, 1122, 1091, 860, 757, 736; HRMS (TOF ES): Found 414.2235, calculated for $C_{24}H_{30}BNO_3Na$ ($M+Na$) 414.2216 (4.6 ppm).



(1*S*,2*R*)-N-benzyl-N-isopropyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54af)

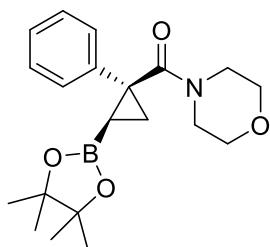
Compound was obtained via typical procedure for dissolved method using N-benzyl-N-isopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**53af**) (72.8 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 82% yield (86.5 mg, 0.206 mmol). *R_f*: 0.48; dr: >98:2; er: 91.5:8.5; $[\alpha]_{\text{D}}^{20}$ 33.14 (*c* = 1.467, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ [7.36 – 7.13 (m), Σ10H], [4.62 (d, *J* = 15.41 Hz) & 4.58 (d, *J* = 16.72 Hz), Σ1H], [4.51 – 4.43 (m) & 4.40 (d, *J* = 15.38 Hz) & 4.15 (d, *J* = 16.48 Hz) & 4.20 – 4.10 (m), Σ2H], [1.81 (dd, *J* = 9.81, 4.14 Hz) & 1.63 (dd, *J* = 9.80, 4.05 Hz), Σ1H], [1.49 (dd, *J* = 7.80, 4.20), Σ1H], [1.30 (s) & 1.23 (s), Σ6H], [1.27 (s) & 1.20 (s), Σ6H], [1.18 (d, *J* = 6.83 Hz) & 0.93 (d, *J* = 6.69), Σ3H], [1.14, (d, *J* = 6.82 Hz) & 0.64 (d, *J* = 6.63 Hz), Σ3H], [0.60 (dd, *J* = 9.81, 7.56 Hz) & 0.55 (dd, *J* = 9.81, 7.78 Hz), Σ1H]; ¹³C (126 MHz, CDCl₃): δ [174.8 & 176.3, Σ1C], [140.4 & 139.9, Σ1C], [139.1 & 136.9, Σ1C], [128.8 & 128.7 & 128.4 & 128.4 & 127.5 & 127.5 & 127.4 & 127.3 & 127.0 & 126.9 & 126.9 & 126.8, (+), Σ10C], [82.2 & 81.7, 2C], [49.8 & 51.2, (+), Σ1C], [45.2 & 50.0, (-), Σ1C], [36.8 & 37.1, Σ1C], [25.1 & 25.2, (+), 2C], [25.0 & 25.1, (+), 2C], 21.6 (+), [20.0 & 19.8, (+), Σ1C], 17.7 (-), 14.3; FTIR (KBr, cm⁻¹): 3060, 3026, 2974, 2931, 1633, 1434, 1404, 1369, 1344, 1323, 1292, 1211, 1145, 1116, 858, 732, 698; HRMS (TOF ES): Found 442.2544, calculated for C₂₆H₃₄BNO₃Na (*M*+Na) 442.2529 (3.4 ppm).



(1S,2R)-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)(piperidin-1-yl)methanone (54aj)

Compound was obtained via typical procedure for dissolved method using (1-phenylcycloprop-2-en-1-yl)(piperidin-1-yl)methanone **(53aj)**

(56.8 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 69% yield (61.4 mg, 0.173 mmol). R_f : 0.16; dr: >98:2; er: 97.5:2.5; $[\alpha]_D^{20}$ 7.77 ($c = 0.733$, CHCl_3); mp: 103.3 – 103.9 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.29 – 7.21 (m, 4H), 7.20 – 7.11 (m, 1H), 3.74 – 3.63 (m, 1H), 3.51 – 3.40 (m, 1H), 3.40 – 3.31 (m, 1H), 3.26 – 3.14 (m, 1H), 1.62 (dd, $J = 9.8, 4.0$ Hz, 1H), 1.58 – 1.50 (m, 4H), 1.47 (dd, $J = 7.7, 4.0$ Hz, 1H), 1.25 (s, 6H), 1.24 – 1.20 (m, 6H), 1.19 – 1.08 (m, 2H), 0.71 (dd, $J = 9.8, 7.6$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 173.7, 140.4, 128.7 (+, 2C), 126.7 (+, 2C), 126.6 (+), 81.9 (2C), 75.1, 47.7 (-), 45.1 (-), 35.8, 25.4 (-), 25.2 (-), 25.0 (+, 4C), 24.2 (-), 19.5 (-), 17.8; FTIR (KBr, cm^{-1}): 2974, 2935, 2856, 1634, 1601, 1468, 1435, 1402, 1371, 1325, 1269, 1209, 1146, 1009, 860, 760, 733, 700; HRMS (TOF ES): Found 378.2223, calculated for $\text{C}_{21}\text{H}_{30}\text{BNO}_3\text{Na}$ ($\text{M}+\text{Na}$) 378.2216 (1.9 ppm).

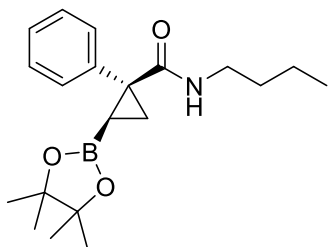


(1S,2R)-morpholino(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methanone (54ak)

Compound was obtained via typical procedure for dissolved method using morpholino(1-phenylcycloprop-2-en-1-yl)methanone **(53ak)**

(57.3 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless oil in 48% yield (43.2 mg, 0.121 mmol). R_f : 0.18; dr: >98:2; er: 94:6; $[\alpha]_D^{20}$ -59.16 ($c = 0.833$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.35 – 7.16 (m, 5H), 3.89 – 3.77 (m,

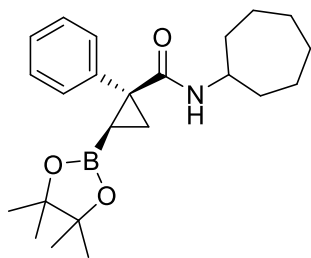
1H), 3.74 – 3.63 (m, 1H), 3.63 – 3.55 (m, 1H), 3.54 – 3.40 (m, 2H), 3.40 – 3.26 (m, 2H), 3.26 – 3.17 (m, 1H), 1.58 (dd, $J = 7.8, 4.0$ Hz, 1H), 1.44 (dd, $J = 9.9, 4.0$ Hz, 1H), 1.27 (s, 6H), 1.24 (s, 6H), 0.81 (dd, $J = 9.9, 7.8$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 171.5, 140.5, 128.9 (+, 2C), 126.8 (+), 126.0 (+, 2C), 83.1 (2C), 66.7 (-), 66.2 (-), 46.6 (-), 43.2 (-), 35.6, 25.3 (+, 2C), 24.9 (+, 2C), 19.6 (-), 13.4; FTIR (KBr, cm^{-1}): 2976, 2924, 2856, 1634, 1601, 1429, 1404, 1371, 1329, 1300, 1273, 1211, 1144, 1115, 1022, 860, 760, 735, 700; HRMS (TOF ES): Found 380.2012, calculated for $\text{C}_{20}\text{H}_{28}\text{BNO}_4\text{Na}$ ($\text{M}+\text{Na}$) 380.2009 (0.8 ppm).



(1S,2R)-N-butyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54am)

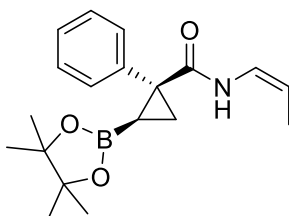
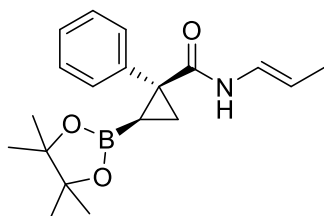
Compound was obtained via typical procedure for dissolved method using N-butyl-1-phenylcycloprop-2-ene-1-carboxamide

(53am) (53.8 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 81% yield (69.3 mg, 0.202 mmol). R_f : 0.41; dr: >98:2; er: 91.5:8.5; $[\alpha]_{\text{D}}^{20}$ -30.55 ($c = 1.100$, CHCl_3); mp: 97.8 – 99.0 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.48 – 7.41 (m, 2H), 7.36 – 7.26 (m, 3H), 5.54 – 5.03 (m, 1H), 3.38 – 2.82 (m, 2H), 1.57 (dd, $J = 8.0, 3.1$ Hz, 1H), 1.38 – 1.32 (m, 2H), 1.32 (s, 6H), 1.29 (s, 6H), 1.25 (dd, $J = 10.2, 3.1$ Hz, 1H), 1.23 – 1.15 (m, 2H), 0.84 (t, $J = 7.3$ Hz, 3H), 0.64 (dd, $J = 10.2, 8.0$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 174.4, 140.0, 131.0 (+, 2C), 128.9 (+, 2C), 127.9 (+), 83.0 (2C), 40.2 (-), 35.8, 31.7 (-), 25.3 (+, 2C), 25.1 (+, 2C), 20.0 (-), 18.8 (-), 13.9 (+), 12.7; FTIR (KBr, cm^{-1}): 3433, 2970, 2929, 2871, 1662, 1647, 1618, 1517, 1436, 1406, 1299, 1211, 1145, 1114, 972, 860, 702; HRMS (TOF ES): Found 366.2215, calculated for $\text{C}_{20}\text{H}_{30}\text{BNO}_3\text{Na}$ ($\text{M}+\text{Na}$) 366.2216 (0.3 ppm).



(1*S*,2*R*)-N-cycloheptyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54an)

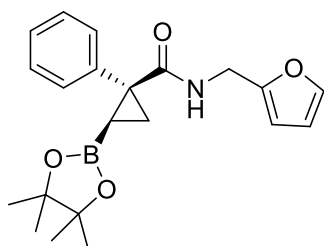
Compound was obtained via typical procedure for dissolved method using N-cycloheptyl-1-phenylcycloprop-2-ene-1-carboxamide (**53an**) (63.8 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous pale yellow oil in 94% yield (90.4 mg, 0.236 mmol). *R*_f: 0.53; dr: >98:2; er: 90.5:9.5; [α]_D²⁰ -23.84 (*c* = 1.233, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.45 – 7.41 (m, 2H), 7.35 – 7.27 (m, 3H), 5.26 (d, *J* = 8.1 Hz, 1H), 3.96 – 3.71 (m, 1H), 1.84 – 1.67 (m, 2H), 1.55 (dd, *J* = 7.9, 3.0 Hz, 1H), 1.54 – 1.47 (m, 2H), 1.47 – 1.34 (m, 7H), 1.31 (s, 6H), 1.28 (s, 6H), 1.27 – 1.21 (m, 1H), 1.24 (dd, *J* = 10.1, 3.0 Hz, 1H), 0.64 (dd, *J* = 10.2, 7.9 Hz, 1H); ¹³C (126 MHz, CDCl₃): δ 173.5, 139.8, 130.9 (+, 2C), 128.8 (+, 2C), 127.9 (+), 82.8 (2C), 51.3 (+), 35.8, 34.8 (-), 34.6 (-), 28.0 (-), 27.8 (-), 25.3 (+, 2C), 25.0 (+, 2C), 24.2 (-), 24.1 (-), 18.7 (-), 13.0; FTIR (KBr, cm⁻¹): 3425, 2974, 2927, 2856, 1660, 1650, 1514, 1444, 1404, 1371, 1301, 1211, 1145, 1112, 975, 960, 860, 765, 703; HRMS (TOF ES): Found 406.2534, calculated for C₂₃H₃₄BNO₃Na (*M*+Na) 406.2529 (1.2 ppm).



(1*S*,2*R*)-1-phenyl-N-((*Z*)-prop-1-en-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ao)

Compound was obtained via typical procedure for dissolved method using N-allyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ao**) (49.8 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1

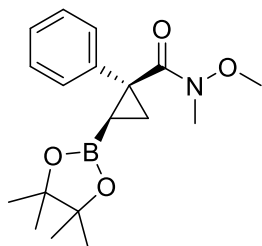
hexane:ethyl acetate mobile phase. The titled compound was obtained as a mixture of isomers in a 1:2 (E:Z) ratio as a colorless oil in 58% yield (47.3 mg, 0.145 mmol). R_f : 0.57; dr: >98:2 for both E and Z isomers; er: 94:6 for both E and Z isomers; $[\alpha]_D^{20}$ -35.73 (c = 0.367, CHCl_3); ^1H NMR (500 MHz, CDCl_3): Major (*Cis* Isomer) δ 7.52 – 7.48 (m, 2H), 7.41 – 7.31 (m, 3H), 6.82 (d, J = 10.9 Hz, 1H), 6.67 – 6.53 (m, 1H), 4.73 – 4.56 (m, 1H), 1.67 (dd, J = 8.3, 3.1 Hz, 1H), 1.32 (s, 6H), 1.30 (s, 6H), 1.33 – 1.31 (m, 1H), 1.20 (dd, J = 7.0, 1.8 Hz, 3H), 0.72 (dd, J = 10.3, 8.3 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 170.9, 139.7, 131.0 (+, 2C), 129.1 (+, 2C), 128.3 (+), 122.4, 104.7, 83.5 (2C), 35.9, 25.2 (+, 2C), 25.1 (+, 2C), 19.2 (-), 12.5, 10.3 (+); FTIR (KBr, cm^{-1}): 3429, 2975, 2929, 1681, 1650, 1487, 1444, 1404, 1371, 1303, 1271, 1213, 1145, 956, 858, 763, 727, 703; HRMS (TOF ES): Found 350.1905, calculated for $\text{C}_{19}\text{H}_{26}\text{BNO}_3\text{Na}$ ($\text{M}+\text{Na}$) 350.1903 (0.6 ppm).



(1*S*,2*R*)-N-(furan-2-ylmethyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ar)

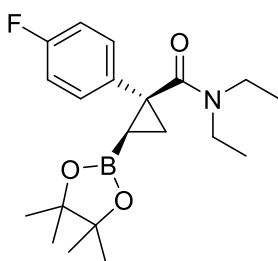
Compound was obtained via typical procedure for dissolved method using N-(furan-2-ylmethyl)-1-phenylcycloprop-2-ene-1-carboxamide (**53ar**) (50.0 mg, 0.21 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 34% yield (26.2 mg, 0.071 mmol). R_f : 0.43; dr: >98:2; er: 93.5:6.5; $[\alpha]_D^{20}$ -35.82 (c = 0.567, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.49 – 7.42 (m, 2H), 7.35 – 7.26 (m, 4H), 6.26 (dd, J = 3.2, 1.8 Hz, 1H), 6.10 (dd, J = 3.2, 1.0 Hz, 1H), 5.68 – 5.56 (m, 1H), 4.34 (dd, J = 5.7, 0.8 Hz, 2H), 1.64 (dd, J = 8.2, 3.1 Hz, 1H), 1.32 (s, 6H), 1.30 – 1.26 (m, 1H), 1.29 (s, 6H), 0.66 (dd, J = 10.2, 8.2 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 173.8, 151.5, 142.0 (+), 139.9, 131.0 (+, 2C), 129.0 (+, 2C), 128.0 (+), 110.4 (+), 107.1 (+), 83.3 (2C), 37.4 (-), 35.8, 25.2 (+, 2C), 25.0 (+, 2C),

18.8 (-), 12.4; FTIR (KBr, cm^{-1}): 3434, 2975, 2929, 1660, 1650, 1519, 1504, 1446, 1407, 1371, 1301, 1211, 1145, 1014, 973, 858, 738, 703; HRMS (TOF ES): Found 390.1855, calculated for $\text{C}_{21}\text{H}_{26}\text{BNO}_4\text{Na}$ ($\text{M}+\text{Na}$) 390.1853 (0.5 ppm).



(1*S*,2*R*)-N-methoxy-N-methyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54au)

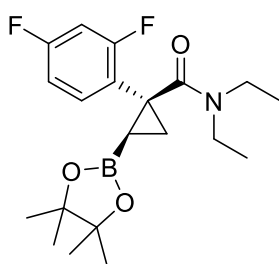
Compound was obtained via typical procedure for dissolved method using N-methoxy-N-methyl-1-phenylcycloprop-2-ene-1-carboxamide (**53au**) (50.8 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 68% yield (56.2 mg, 0.170 mmol). R_f : 0.40; dr: 97:3; er: 94.5:5.5; $[\alpha]_{\text{D}}^{20}$ -64.64 ($c = 0.733$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.37 – 7.29 (m, 2H), 7.30 – 7.23 (m, 2H), 7.21 – 7.14 (m, 1H), 3.12 (s (broad), 6H), 1.58 (dd, $J = 7.8, 3.8$ Hz, 1H), 1.26 (s, 6H), 1.26 - 1.25 (m, 1H), 1.25 (s, 6H), 0.84 (dd, $J = 9.9, 7.8$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 174.2, 141.0, 128.4 (+, 2C), 127.8 (+), 126.7 (+, 2C), 83.3 (2C), 60.4 (-), 36.0, 33.5 (+), 25.1 (+, 2C), 24.9 (+, 2C), 18.6, 10.0 (+); FTIR (KBr, cm^{-1}): 2975, 2933, 1666, 1650, 1444, 1407, 1371, 1328, 1298, 1211, 1164, 1145, 1122, 1004, 975, 860, 763, 700; HRMS (TOF ES): Found 354.1866, calculated for $\text{C}_{18}\text{H}_{26}\text{BNO}_4\text{Na}$ ($\text{M}+\text{Na}$) 354.1853 (3.7 ppm).



(1*S*,2*R*)-N,N-diethyl-1-(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ba)

Compound was obtained via typical procedure for dissolved method using N,N-diethyl-1-(4-fluorophenyl)cycloprop-2-ene-1-carboxamide (**53ba**) (58.3 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was

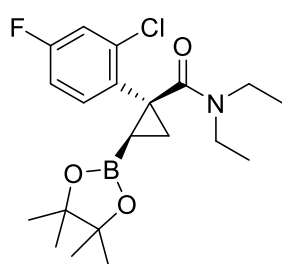
purified by column chromatography using 1:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 88% yield (79.8 mg, 0.220 mmol). R_f : 0.33; dr: >98:2; er: 90:10; $[\alpha]_D^{20}$ 38.80 ($c = 1.533$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.32 – 7.19 (m, 2H), 7.00 – 6.86 (m, 2H), 3.44 – 3.30 (m, 2H), 3.22 (q, $J = 7.2$ Hz, 2H), 1.58 (dd, $J = 9.9, 3.9$ Hz, 1H), 1.42 (dd, $J = 7.5, 4.0$ Hz, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.14 (t, $J = 7.1$ Hz, 3H), 0.72 (t, $J = 7.1$ Hz, 3H), 0.60 (dd, $J = 9.9, 7.6$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 174.8, 161.7 (d, $J = 245.8$ Hz), 136.1 (d, $J = 3.1$ Hz), 129.3 (+, dd, $J = 8.1, 2.2$ Hz, 2C), 115.6 (+, d, $J = 21.4$ Hz, 2C), 81.6 (2C), 42.9 (-), 41.9 (-), 35.5, 25.1 (+, 2C), 25.1 (+, 2C), 19.6 (-), 18.1, 12.8 (+), 12.6 (+); ^{19}F NMR (376 MHz, CDCl_3) δ -115.50 (s, 1F); FTIR (KBr, cm^{-1}): 3066, 2974, 2935, 2875, 1631, 1602, 1512, 1458, 1431, 1004, 1380, 1323, 1290, 1272, 1220, 1143, 1116, 952, 860, 835, 821; HRMS (TOF ES): Found 384.2126, calculated for $\text{C}_{20}\text{H}_{29}\text{BFNO}_3\text{Na}$ ($\text{M}+\text{Na}$) 384.2122 (1.0 ppm).



(1S,2R)-1-(2,4-difluorophenyl)-N,N-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ca)

Compound was obtained via typical procedure for dissolved method using 1-(2,4-difluorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (**53ca**) (62.8 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 1:2 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 96% yield (91.0 mg, 0.240 mmol). R_f : 0.24; dr: >98:2; er: 95.5:4.5; $[\alpha]_D^{20}$ 104.58 ($c = 1.900$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.33 – 7.26 (m, 1H), 6.88 – 6.71 (m, 2H), 3.56 – 3.40 (m, 1H), 3.35 – 3.24 (m, 2H), 3.22 – 3.09 (m, 1H), 1.70 (dd, $J = 10.0, 4.1$ Hz, 1H), 1.43 (dd, $J = 7.6, 4.1$ Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.16 (t, $J = 7.1$ Hz, 3H), 0.74 (t, $J = 7.1$ Hz, 3H), 0.62 (dd, $J = 10.0, 7.6$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 176.2, 162.2 (dd, $J = 249.5, 11.8$ Hz), 162.0

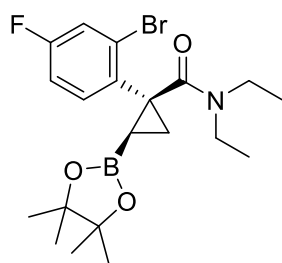
(dd, $J = 251.2, 11.9$ Hz) 131.1 (+, dd, $J = 9.5, 5.0$ Hz), 123.5 (dd, $J = 13.7, 3.9$ Hz), 111.7 (+, dd, $J = 21.2, 3.6$ Hz), 104.4 (+, t, $J = 25.3$ Hz), 80.8 (2C), 43.2 (-), 43.2 (-), 30.3, 25.3 (+, 2C), 25.1 (+, 2C), 20.3, 19.7 (-), 12.7 (+), 12.5 (+); ^{19}F NMR (376 MHz, CDCl_3) δ -108.1 (d, $J = 7.6$ Hz, 1F), -110.6 (d, $J = 7.4$ Hz, 1F); FTIR (KBr, cm^{-1}): 2974, 2937, 1607, 1506, 1462, 1385, 1350, 1271, 1184, 1140, 1115, 1088, 974, 851, 808, 721, 675; HRMS (TOF ES): Found 402.2032, calculated for $\text{C}_{20}\text{H}_{28}\text{BF}_2\text{NO}_3\text{Na}$ ($\text{M}+\text{Na}$) 402.2028 (1.0 ppm).



(1*S*,2*R*)-1-(2-chloro-4-fluorophenyl)-*N,N*-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54da)

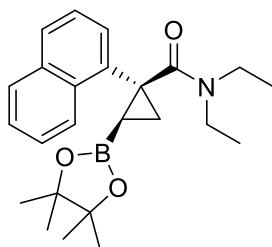
Compound was obtained via typical procedure for dissolved method using 1-(2-chloro-4-fluorophenyl)-*N,N*-diethylcycloprop-2-ene-1-carboxamide (**53da**) (67.0 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 1:2 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 85% yield (84.0 mg, 0.212 mmol). R_f : 0.17; dr: >98:2; er: 97:3; $[\alpha]_{\text{D}}^{20}$ 139.08 ($c = 1.667$, CHCl_3); mp: 100.0 – 101.6 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.30 (dd, $J = 8.7, 5.9$ Hz, 1H), 7.11 (dd, $J = 8.3, 2.7$ Hz, 1H), 6.94 (td, $J = 8.2, 2.7$ Hz, 1H), 3.74 – 3.52 (m, 1H), 3.32 – 3.08 (m, 2H), 3.09 – 2.96 (m, 1H), 1.75 (dd, $J = 10.0, 4.1$ Hz, 1H), 1.45 (dd, $J = 7.4, 4.0$ Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.19 (t, $J = 7.1$ Hz, 3H), 0.75 (t, $J = 7.1$ Hz, 3H), 0.62 (dd, $J = 9.9, 7.4$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 176.7, 161.6 (d, $J = 250.5$ Hz), 137.9 (d, $J = 10.3$ Hz), 134.0 (d, $J = 3.6$ Hz), 131.1 (+, d, $J = 8.7$ Hz), 117.3 (+, d, $J = 24.6$ Hz), 114.4 (+, d, $J = 21.0$ Hz), 80.3 (2C), 44.2 (-), 43.9 (-), 34.2, 25.7 (+, 2C), 25.0 (+, 2C), 21.8 (-), 21.1, 12.6 (+), 12.5 (+); ^{19}F NMR (376 MHz, CDCl_3) δ -112.4 (s, 1F); FTIR (KBr, cm^{-1}): 2972, 2937, 1715, 1601, 1495, 1454, 1385, 1346, 1265, 1209,

1184, 1159, 1115, 910, 858, 806, 754, 675; HRMS (TOF ES): Found 402.2006, calculated for $C_{20}H_{28}BF_2NO_3Na$ ($M+Na$) 402.2028 (5.5 ppm).



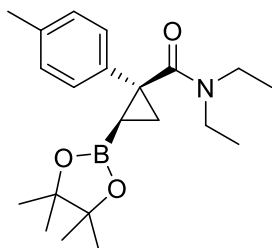
(1S,2R)-1-(2-bromo-4-fluorophenyl)-N,N-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ea)

Compound was obtained via typical procedure for dissolved method using 1-(2-bromo-4-fluorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (**53ea**) (78.0 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 98% yield (108 mg, 0.245 mmol). R_f : 0.17; dr: >98:2; er: 95:5; $[\alpha]_D^{20}$ 105.18 ($c = 2.767$, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 2H), 7.01 – 6.95 (m, 1H), 3.78 – 3.50 (m, 1H), 3.33 – 3.09 (m, 2H), 3.09 – 2.93 (m, 1H), 1.75 (dd, $J = 10.0, 4.0$ Hz, 1H), 1.50 (dd, $J = 7.4, 4.0$ Hz, 1H), 1.23 (s, 6H), 1.23 (s, 6H), 1.20 (t, $J = 7.2$ Hz, 3H), 0.75 (t, $J = 7.1$ Hz, 3H), 0.65 (dd, $J = 10.0, 7.4$ Hz, 1H); ^{13}C (126 MHz, $CDCl_3$): δ 176.6, 161.5 (d, $J = 251.7$ Hz), 135.6 (d, $J = 3.6$ Hz), 131.6 (+, d, $J = 8.5$ Hz), 127.7 (d, $J = 9.5$ Hz), 120.6 (+, d, $J = 24.2$ Hz), 114.9 (+, d, $J = 21.0$ Hz), 80.3 (2C), 44.4 (-), 43.9 (-), 36.1, 25.6 (+, 2C), 25.0 (+, 2C), 22.4, 22.0 (-), 12.6 (+), 12.5 (+); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.5 (s, 1F); FTIR (KBr, cm^{-1}): 2972, 2935, 1596, 1488, 1461, 1440, 1382, 1344, 1265, 1209, 1157, 1112, 1099, 1035, 972, 946, 864, 806, 707; HRMS (TOF ES): Found 462.1229, calculated for $C_{20}H_{28}BBFNO_3Na$ ($M+Na$) 462.1227 (0.4 ppm).



(1S,2R)-N,N-diethyl-1-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54fa)

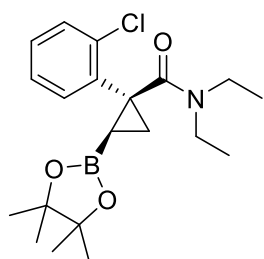
Compound was obtained via typical procedure for dissolved method using N,N-diethyl-1-(naphthalen-1-yl)cycloprop-2-ene-1-carboxamide (**53fa**) (66.3 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 88% yield (86.8 mg, 0.221 mmol). R_f : 0.19; dr: >98:2; er: 94.5:5.5; $[\alpha]_D^{20}$ 151.77 ($c = 1.867$, CHCl_3); mp: 109.8 – 110.5 °C; ^1H NMR (500 MHz, CDCl_3): δ 8.39 (d, $J = 8.5$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.62 – 7.53 (m, 1H), 7.52 – 7.42 (m, 2H), 7.41 – 7.32 (m, 1H), 3.64 – 3.50 (m, 1H), 3.19 – 3.02 (m, 2H), 2.97 – 2.80 (m, 1H), 1.95 – 1.81 (m, 1H), 1.59 – 1.50 (m, 1H), 1.31 (s, 6H), 1.27 (s, 6H), 1.08 (t, $J = 7.1$ Hz, 3H), 0.78 – 0.63 (m, 1H), 0.37 (t, $J = 7.1$ Hz, 3H); ^{13}C (126 MHz, CDCl_3): δ 177.5, 136.3, 133.8, 133.6, 128.4 (+), 128.2 (+), 127.1 (+), 126.2 (+), 125.8 (+), 125.6 (+), 125.3 (+), 80.6 (2C), 44.1 (-), 43.6 (-), 34.3, 25.8 (+, 2C), 25.1 (+, 2C), 20.6 (-), [12.6 & 12.4, (+), $\Sigma 3\text{C}$]; FTIR (KBr, cm^{-1}): 3045, 2972, 2933, 1595, 1458, 1438, 1380, 1361, 1340, 1282, 1211, 1188, 1114, 972, 902, 802, 781, 736, 703, 676, 638; HRMS (TOF ES): Found 416.2359, calculated for $\text{C}_{24}\text{H}_{32}\text{BNO}_3\text{Na}$ ($\text{M}+\text{Na}$) 416.2373 (3.4 ppm).



(1S,2R)-N,N-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)cyclopropane-1-carboxamide (54ga)

Compound was obtained via typical procedure for dissolved method using N,N-diethyl-1-(p-tolyl)cycloprop-2-ene-1-carboxamide (**53ga**) (57.3 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound

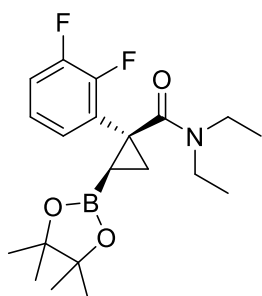
was obtained as a very viscous pale yellow oil in 92% yield (81.8 mg, 0.229 mmol). R_f : 0.21; dr: >98:2; er: 91:9; $[\alpha]_D^{20}$ 44.62 ($c = 1.300$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.17 (d, $J = 8.2$ Hz, 2H), 7.06 (d, $J = 7.7$ Hz, 2H), 3.48 – 3.29 (m, 2H), 3.28 – 3.15 (m, 2H), 2.29 (s, 3H), 1.62 (dd, $J = 9.8$, 3.9 Hz, 1H), 1.39 (dd, $J = 7.4$, 3.9 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.16 (t, $J = 7.1$ Hz, 3H), 0.73 (t, $J = 7.1$ Hz, 3H), 0.62 (dd, $J = 9.8$, 7.4 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 175.8, 137.1, 136.5, 129.4 (+, 2C), 127.8 (+, d, $J = 2.0$ Hz, 2C), 81.3 (2C), 43.1 (-), 42.2 (-), 35.7, 25.2 (+, 2C), 25.2 (+, 2C), 21.2 (+), 19.6 (-), 18.9, 12.8 (+), 12.6 (+); FTIR (KBr, cm^{-1}): 2974, 2933, 2873, 1633, 1598, 1515, 1496, 1427, 1402, 1380, 1371, 1323, 1288, 1271, 1209, 1145, 1114, 952, 860, 808; HRMS (TOF ES): Found 380.2365, calculated for $\text{C}_{21}\text{H}_{32}\text{BNO}_3\text{Na}$ ($\text{M}+\text{Na}$) 380.2373 (2.1 ppm).



(1S,2R)-1-(2-chlorophenyl)-N,N-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ia)

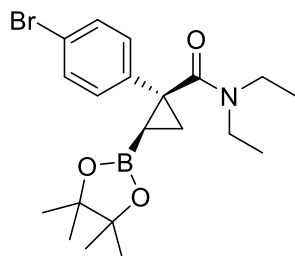
Compound was obtained via typical procedure for dissolved method using 1-(2-chlorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (**53ia**) (62.4 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow solid in 96% yield (90.6 mg, 0.240 mmol). R_f : 0.17; dr: >98:2; er: 87.5:12.5; $[\alpha]_D^{20}$ 140.64 ($c = 2.233$, CHCl_3); mp: 140.5 – 142.8 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.38 – 7.28 (m, 2H), 7.23 – 7.15 (m, 2H), 3.72 – 3.59 (m, 1H), 3.31 – 3.08 (m, 2H), 3.09 – 2.92 (m, 1H), 1.80 (dd, $J = 9.9$, 4.0 Hz, 1H), 1.43 (dd, $J = 7.4$, 4.0 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.19 (t, $J = 7.2$ Hz, 3H), 0.72 (t, $J = 7.1$ Hz, 3H), 0.64 (dd, $J = 10.0$, 7.3 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 177.1, 137.8, 137.1, 130.0 (+, 2C), 128.6 (+), 127.2 (+), 80.1 (2C), 44.2 (-), 43.9 (-), 34.8, 25.7 (+, 2C), 25.0 (+, 2C), 21.9, 20.9 (-), 12.5 (+), 12.5 (+); FTIR (KBr, cm^{-1}): 2970, 2937, 1600, 1485, 1461,

1438, 1382, 1346, 1284, 1245, 1186, 1157, 1114, 1051, 972, 904, 757, 671; HRMS (TOF ES): Found 400.1825, calculated for $C_{20}H_{29}BClNO_3Na$ ($M+Na$) 400.1827 (0.5 ppm).



(1*S*,2*R*)-1-(2,3-difluorophenyl)-*N,N*-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ja)

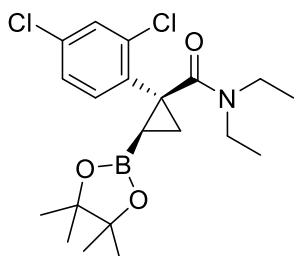
Compound was obtained via typical procedure for dissolved method using 1-(2,3-difluorophenyl)-*N,N*-diethylcycloprop-2-ene-1-carboxamide (**53ja**) (63.0 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow solid in 91% yield (86.1 mg, 0.227 mmol). R_f : 0.24; dr: >98:2; er: 91.5:8.5; $[\alpha]_D^{20}$ 103.46 ($c = 1.300$, $CHCl_3$); mp: 99.9 – 101.3 °C; 1H NMR (500 MHz, $CDCl_3$): δ 7.09 – 6.97 (m, 3H), 3.60 – 3.41 (m, 1H), 3.38 – 3.22 (m, 2H), 3.22 – 3.10 (m, 1H), 1.76 (dd, $J = 10.0, 4.2$ Hz, 1H), 1.44 (dd, $J = 7.6, 4.2$ Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H), 1.17 (t, $J = 7.1$ Hz, 3H), 0.76 (t, $J = 7.1$ Hz, 3H), 0.67 (dd, $J = 10.0, 7.6$ Hz, 1H); ^{13}C (126 MHz, $CDCl_3$): δ 175.9, 150.8 (dd, $J = 243.7, 6.4$ Hz), 150.0 (dd, $J = 248.7, 11.5$ Hz), 129.8 (d, $J = 10.2$ Hz), 124.5 (+, t, $J = 2.7$ Hz), 124.4 (+, dd, $J = 7.1, 4.7$ Hz), 116.3 (+, d, $J = 17.1$ Hz), 80.8 (2C), 43.3 (-), 43.2 (-), 30.7 (t, $J = 2.3$ Hz), 25.3 (+, 2C), 25.1 (+, 2C), 20.6, 19.8 (-), 12.6 (+), 12.5 (+); ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.6 (d, $J = 20.5$ Hz, 1F), -138.4 (d, $J = 20.5$ Hz, 1F); FTIR (KBr, cm^{-1}): 2974, 2937, 1631, 1604, 1479, 1442, 1406, 1382, 1323, 1292, 1263, 1211, 1141, 1114, 968, 862, 788, 729, 667; HRMS (TOF ES): Found 402.2026, calculated for $C_{20}H_{28}BF_2NO_3Na$ ($M+Na$) 402.2028 (0.5 ppm).



(1S,2R)-1-(4-bromophenyl)-N,N-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54la)

Compound was obtained via typical procedure for dissolved method using 1-(4-bromophenyl)-N,N-diethylcycloprop-2-ene-1-

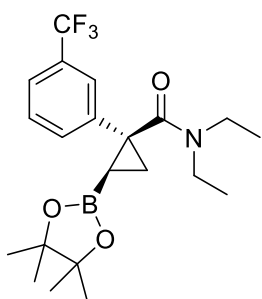
carboxamide **(53la)** (74.0 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 85% yield (89.9 mg, 0.213 mmol). *R*_f: 0.17; dr: >98:2; er: 87:13; [α]_D²⁰ 21.25 (*c* = 1.600, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.43 – 7.34 (m, 2H), 7.19 – 7.09 (m, 2H), 3.46 – 3.30 (m, 2H), 3.30 – 3.14 (m, 2H), 1.59 (dd, *J* = 9.9, 4.0 Hz, 1H), 1.44 (dd, *J* = 7.6, 4.0 Hz, 1H), 1.25 (s, 6H), 1.22 (s, 6H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 7.1 Hz, 3H), 0.62 (dd, *J* = 9.9, 7.6 Hz, 1H); ¹³C (126 MHz, CDCl₃): δ 174.2, 139.6, 131.8 (+, 2C), 129.1 (+, 2C), 120.6, 81.8 (2C), 42.9 (-), 41.8 (-), 35.7, 25.1 (+, 2C), 25.1 (+, 2C), 19.5 (-), 18.1, 12.9 (+), 12.6 (+); FTIR (KBr, cm⁻¹): 2974, 2933, 2873, 1633, 1600, 1490, 1460, 1427, 1406, 1388, 1323, 1288, 1267, 1213, 1139, 1116, 1008, 860, 808; HRMS (TOF ES): Found 444.1321, calculated for C₂₀H₂₉BBrNO₃Na (*M*+Na) 444.1322 (0.2 ppm).



(1S,2R)-1-(2,4-dichlorophenyl)-N,N-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54ma)

Compound was obtained via typical procedure for dissolved method using 1-(2,4-dichlorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide **(53ma)** (76.0 mg, 0.267 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow amorphous solid in 98% yield (108 mg, 0.262 mmol). *R*_f: 0.14; dr: >98:2;

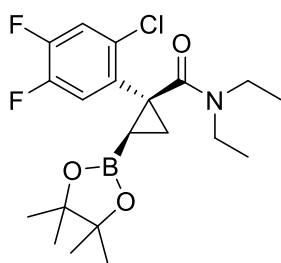
er: 98:2; $[\alpha]_{\text{D}}^{20}$ 132.12 ($c = 2.433$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.37 (d, $J = 2.2$ Hz, 1H), 7.25 (d, $J = 9.2$ Hz, 1H), 7.19 (dd, $J = 8.3, 2.1$ Hz, 1H), 3.71 – 3.58 (m, 1H), 3.26 – 3.09 (m, 2H), 3.09 – 2.97 (m, 1H), 1.75 (dd, $J = 10.0, 4.1$ Hz, 1H), 1.46 (dd, $J = 7.4, 4.1$ Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.18 (t, $J = 7.2$ Hz, 3H), 0.77 (t, $J = 7.1$ Hz, 3H), 0.63 (dd, $J = 10.0, 7.4$ Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 176.5, 137.8, 136.6, 133.8, 130.7 (+), 129.7 (+), 127.5 (+), 80.3 (2C), 44.2 (-), 43.9 (-), 34.3, 25.6 (+, 2C), 25.0 (+, 2C), 21.8, 21.0 (-), 12.6 (+), 12.5 (+); FTIR (KBr, cm^{-1}): 2972, 2935, 1600, 1483, 1461, 1444, 1380, 1361, 1344, 1280, 1157, 1114, 1107, 972, 904, 867, 815, 777, 659; HRMS (TOF ES): Found 434.1436, calculated for $\text{C}_{20}\text{H}_{28}\text{BCl}_2\text{NO}_3\text{Na}$ ($\text{M}+\text{Na}$) 434.1437 (0.2 ppm).



(1S,2R)-N,N-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3-(trifluoromethyl)phenyl)cyclopropane-1-carboxamide (54na)

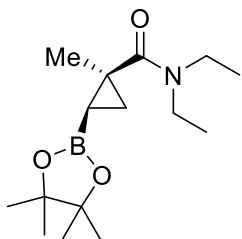
Compound was obtained via typical procedure for dissolved method using N,N-diethyl-1-(3-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxamide (**53na**) (71.0 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 1:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 87% yield (89.6 mg, 0.218 mmol). R_f : 0.24; dr: >98:2; er: 91.5:8.5; $[\alpha]_{\text{D}}^{20}$ 9.55 ($c = 1.100$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.51 – 7.42 (m, 3H), 7.42 – 7.36 (m, 1H), 3.45 – 3.31 (m, 2H), 3.32 – 3.12 (m, 2H), 1.64 (dd, $J = 9.9, 4.2$ Hz, 1H), 1.53 (dd, $J = 7.7, 4.1$ Hz, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.16 (t, $J = 7.1$ Hz, 3H), 0.73 (t, $J = 7.1$ Hz, 3H), 0.72 – 0.67, 1H); ^{13}C (126 MHz, CDCl_3): δ 173.4, 141.7, 131.1 (q, $J = 32.2$ Hz), 130.7 (+), 129.3 (+), 124.1 (q, $J = 272.4$ Hz), 123.6 (+, d, $J = 2.3$ Hz), 123.6 (+, d, $J = 2.3$ Hz), 82.2 (2C), 42.8 (-), 41.5 (-), 36.0, 25.1 (+, 2C), 25.0 (+, 2C), 19.6 (-), 17.7, 12.7 (+), 12.6 (+); ^{19}F NMR (376 MHz, CDCl_3) δ -62.6 (s, 3F); FTIR (KBr, cm^{-1}): 2975, 2935, 2877, 1639, 1460, 1427, 1404, 1371, 1332,

1274, 1213, 1166, 1126, 1076, 964, 860, 800, 702; HRMS (TOF ES): Found 434.2099, calculated for $C_{21}H_{29}BF_3NO_3Na$ ($M+Na$) 434.2090 (2.1 ppm).



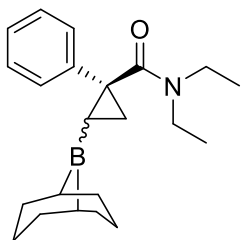
(1S,2R)-1-(2-chloro-4,5-difluorophenyl)-N,N-diethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (54oa)

Compound was obtained via typical procedure for dissolved method using 1-(2-chloro-4,5-difluorophenyl)-N,N-diethylcycloprop-2-ene-1-carboxamide (**53oa**) (71.0 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 91% yield (94.1 mg, 0.227 mmol). R_f : 0.28; dr: >98:2; er: 97:3; $[\alpha]_D^{20}$ 121.78 ($c = 2.300$, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$): δ 7.20 (dd, $J = 9.7, 7.3$ Hz, 1H), 7.15 (dd, $J = 10.8, 8.1$ Hz, 1H), 3.75 – 3.54 (m, 1H), 3.29 – 3.11 (m, 2H), 3.11 – 2.98 (m, 1H), 1.70 (dd, $J = 10.1, 4.2$ Hz, 1H), 1.47 (dd, $J = 7.5, 4.2$ Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.19 (t, $J = 7.2$ Hz, 3H), 0.80 (t, $J = 7.1$ Hz, 3H), 0.64 (dd, $J = 10.1, 7.5$ Hz, 1H); ^{13}C (126 MHz, $CDCl_3$): δ 175.8, 149.1 (dd, $J = 253.1, 13.5$ Hz), 148.9 (dd, $J = 250.0, 12.5$ Hz), 134.8 (t, $J = 4.7$ Hz), 131.8 (dd, $J = 7.7, 3.6$ Hz), 118.9 (+, d, $J = 20.0$ Hz), 118.1 (+, d, $J = 18.7$ Hz), 80.3 (2C), 44.0 (-), 43.8 (-), 34.2, 25.5 (+, 2C), 24.8 (+, 2C), 21.9, 21.0 (-), 12.5 (+), 12.4 (+); ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.9 (d, $J = 21.7$ Hz, 1F), -137.7 (d, $J = 21.7$ Hz, 1F); FTIR (KBr, cm^{-1}): 2972, 2937, 2879, 1600, 1496, 1463, 1442, 1404, 1382, 1361, 1340, 1292, 1267, 1238, 1217, 1184, 1114, 792, 707; HRMS (TOF ES): Found 436.1639, calculated for $C_{20}H_{27}BClF_2NO_3Na$ ($M+Na$) 436.1638 (0.2 ppm).



(1*S*,2*R*)-*N,N*-diethyl-1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1-carboxamide (57)

Compound was obtained via typical procedure for dissolved method using *N,N*-diethyl-1-methylcycloprop-2-ene-1-carboxamide (**56**) (76.6 mg, 0.50 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 92% yield (128 mg, 0.46 mmol). *R*_f: 0.17; dr: >98:2; er: 92:8; [α]_D²⁰ +49.51 (*c* = 0.80, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 3.61 (dq, *J* = 14.4, 7.2 Hz, 1H), 3.46 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.39 – 3.23 (m, 2H), 1.36 (s, 3H), 1.23 – 1.19 (m, 3H), 1.19 (s, 6H), 1.17 (s, 6H), 1.13 (dd, *J* = 7.0, 3.6 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.83 (dd, *J* = 9.4, 3.6 Hz, 1H), 0.18 (dd, *J* = 9.4, 7.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 175.0, 82.0, 42.1 (-), 40.9 (-), 27.1, 25.1 (+, 4C), 22.7 (+), 20.1 (-), 14.1 (+), 13.8 (+, broad), 12.7 (+); FTIR (KBr, cm⁻¹): 2975, 2934, 1635, 1428, 1408, 1324, 1240, 1146, 1130, 973, 860; HRMS (TOF ES): Found 278.2651, calculated for C₁₇H₃₃BNO (*M*+*H*) 278.2655 (1.4 ppm).

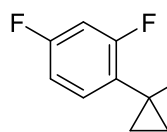


2-(9-borabicyclo[3.3.1]nonan-9-yl)-*N,N*-diethyl-1-phenylcyclopropane-1-carboxamide (66/67)

Compound was obtained via typical procedure for dissolved method using *N,N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (108.0 mg, 0.50 mmol, 1.0 equiv.) and 9-Borabicyclo[3.3.1]nonane dimer (1.0 mL, 0.5M in THF, 0.50 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 53% yield (89.6 mg, 0.266 mmol). *R*_f: 0.31; dr: 70:30; ¹H NMR (500 MHz, CDCl₃): **Major**: δ 7.32 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 3.48 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.35 (dq,

$J = 14.0, 7.1$ Hz, 1H), 3.26 (dq, $J = 14.4, 7.2$ Hz, 1H), 3.07 (dq, $J = 14.2, 7.1$ Hz, 1H), 1.99 – 1.88 (m, 2H), 1.86 – 1.80 (m, 3H), 1.76 – 1.66 (m, 5H), 1.54 (s, 2H), 1.46 – 1.40 (m, 1H), 1.21 (t, $J = 7.1$ Hz, 3H), 1.00 – 0.93 (m, 2H), 0.73 (t, $J = 7.1$ Hz, 3H), 0.69 – 0.64 (m, 1H), 0.50 – 0.42 (m, 1H). **Minor:** δ 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 2H), 7.11 – 7.06 (m, 1H), 3.74 – 3.38 (m, 4H), 1.95 (dd, $J = 8.4, 2.8$ Hz, 1H), 1.92 – 1.82 (m, 3H), 1.82 – 1.73 (m, 1H), 1.71 – 1.61 (m, 3H), 1.54 (s, 2H), 1.45 (dd, $J = 8.4, 2.7$ Hz, 1H), 1.34 (t, $J = 7.2$ Hz, 3H), 1.26 – 1.23 (m, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.22 – 1.16 (m, 1H), 1.13 – 1.05 (m, 1H), 0.77 – 0.71 (m, 1H), 0.71 – 0.61 (m, 1H), 0.59 – 0.53 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3): **Major:** δ 179.8, 140.8, 129.0 (+, 2C), 128.9 (+, 2C), 126.7 (+), 44.4 (-), 43.7 (-), 36.1, 33.6 (-), 32.7 (-), 32.4 (-), 31.8 (-), 28.0 (+), 27.9 (+), 25.9 (-), 25.5 (-), 18.8 (-), 12.6 (+), 12.5(+), 12.2 (+). **Minor:** δ 178.9, 148.3, 129.8 (+, 2C), 127.8 (+, 2C), 124.8 (+), 44.8 (-), 43.0 (-), 33.0 (-), 32.7 (-), 32.5 (-), 31.0 (-), 27.1, 27.0 (+), 26.9 (+), 25.6 (-), 25.0 (-), 21.5 (-), 14.3 (+), 13.0 (+), 12.9 (+); FTIR (KBr, cm^{-1}): 2978, 2914, 2869, 2835, 1600, 1488, 1314, 1212, 968, 759, 726, 700; HRMS (TOF ES): Found 338.2650, calculated for $\text{C}_{22}\text{H}_{33}\text{BNO}$ ($\text{M}+\text{H}$) 338.2655 (1.5 ppm).

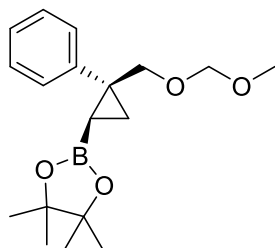
2.12.6 Miscellaneous Catalytic Asymmetric Hydroboration



(1-(3,4-difluorophenyl)cyclopropyl)methanol

Compound was obtained via typical procedure for dissolved method using (1-(2,4-difluorophenyl)cycloprop-2-en-1-yl)methanol (###) (45.5 mg, 0.25 mmol, 1.0 equiv.). The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 49% yield (22.5 mg, 0.122 mmol). R_f : 0.22; ^1H NMR (500 MHz, CDCl_3): δ 7.34 – 7.27 (m, 1H), 6.90 – 6.73 (m, 2H), 3.60 (s, 2H), 1.47 (s, 1H), 0.92 – 0.76 (m, 4H); ^{13}C (126 MHz, CDCl_3): δ 162.6 (dd, $J = 249.5, 11.8$ Hz), 162.1 (dd, $J = 247.7, 12.0$ Hz), 133.2 (+, dd, $J = 9.6, 6.0$ Hz), 125.6 (dd, $J = 14.1, 3.7$ Hz), 111.1 (+, dd, $J = 20.9, 3.6$

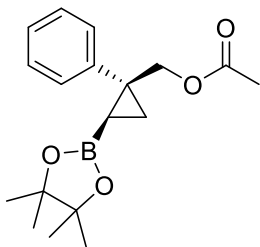
Hz), 105.5 – 101.5 (+, m), 70.4 (-), 23.6, 10.3 (-, d, $J = 1.7$ Hz, 2C); FTIR (KBr, cm^{-1}): 3354, 3082, 3007, 2928, 2872, 1614, 1601, 1506, 1466, 1421, 1267, 1138, 1117, 1084, 1036, 968, 849, 816, 734; HRMS (TOF ES): Found 235.0558, calculated for $\text{C}_{11}\text{H}_{10}\text{F}_2\text{O}_2\text{Na}$ ($\text{M}+\text{Na}$) 235.0547 (4.7 ppm).



**2-((1R,2S)-2-((methoxymethoxy)methyl)-2-phenylcyclopropyl)-
4,4,5,5-tetramethyl-1,3,2-dioxaborolane (44)**

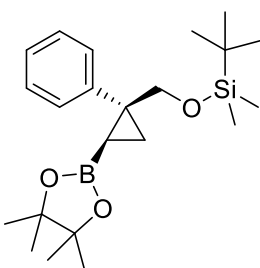
Compound was obtained via typical procedure for dissolved method using (1-((methoxymethoxy)methyl)cycloprop-2-en-1-yl)benzene (**40**)

(95.2 mg, 0.50 mmol, 1.0 equiv.), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (14.8 mg, 0.03 μmol , 0.06 equiv.) and (R)-BINAP (37.4.0 mg, 0.06 mmol, 0.12 equiv.), Pinnacol borane (148.0 μL , 1.0 mmol, 2.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 20:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless oil in 81% yield (128.2 mg, 0.402 mmol). R_f : 0.31; dr: 98:2; er: 68:32; $[\alpha]_{\text{D}}^{20} +10.58$ ($c = 1.04$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.38 (m, 2H), 7.31 – 7.25 (m, 2H), 7.21 – 7.16 (m, 1H), 4.53 (s, 2H), 3.96 (d, $J = 10.1$ Hz, 1H), 3.70 (d, $J = 10.1$ Hz, 1H), 3.14 (s, 3H), 1.29 (s, 6H), 1.28 (s, 6H), 1.22 (dd, $J = 9.5, 3.8$ Hz, 1H), 1.12 (dd, $J = 7.3, 3.8$ Hz, 1H), 0.47 (dd, $J = 9.5, 7.3$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 144.7, 128.9 (+, 2C), 128.1 (+, 2C), 126.3 (+), 96.3 (-), 83.4 (2C), 72.8 (-), 55.1 (+), 32.3, 25.1 (+, 2C), 24.8 (+, 2C), 17.6 (-), 7.3 (+); FTIR (KBr, cm^{-1}): 2978, 2929, 2882, 1415, 1371, 1323, 1215, 1147, 1106, 1053, 966, 859, 700; HRMS (TOF ES): Found 337.2322, calculated for $\text{C}_{20}\text{H}_{31}\text{BO}_2\text{Na}$ ($\text{M}+\text{Na}$) 337.2315 (2.1 ppm).



(1S*,2R*)- (1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methyl acetate (45)

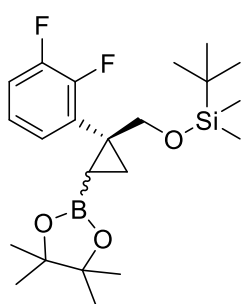
Compound was obtained via typical procedure for dissolved method using (1-phenylcycloprop-2-en-1-yl)methyl acetate **(41)** (47.1 mg, 0.25 mmol, 1.0 equiv.) and allowing the reaction to stir overnight. The product was purified by column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 83% yield (65.0 mg, 0.206 mmol). R_f : 0.29; dr: 96:4; er: 79:21; $[\alpha]_D^{20}$ -45.65 (c = 1.233, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.37 – 7.32 (m, 2H), 7.30 – 7.24 (m, 2H), 7.22 – 7.17 (m, 1H), 4.51 (d, J = 11.41 Hz, 1H), 4.19 (d, J = 11.4 Hz, 1H), 1.97 (s, 3H), 1.27 (s, 6H), 1.24 (s, 6H), 1.24 – 1.19 (m, 1H), 1.15 (dd, J = 7.3, 3.9 Hz, 1H), 0.51 (dd, J = 9.6, 7.3 Hz, 1H); ^{13}C (126 MHz, CDCl_3): δ 171.1, 143.8, 129.0 (+, 2C), 128.2 (+, 2C), 126.7 (+), 83.5 (2C), 70.2 (-), 31.1, 25.1 (+, 2C), 24.6 (+, 2C), 21.2 (+), 17.9 (-), 7.3; FTIR (KBr, cm^{-1}): 3059, 2978, 2934, 1742, 1732, 1416, 1371, 1362, 1327, 1248, 1215, 1167, 1144, 1028, 976, 858, 729, 700, 671; HRMS (TOF ES): Found 339.1745, calculated for $\text{C}_{18}\text{H}_{25}\text{BO}_4\text{Na}$ ($\text{M}+\text{Na}$) 339.1744 (0.3 ppm).



(1S*,2R*)-tert-butyldimethyl((1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methoxy)silane (46)

Compound was obtained via typical procedure for dissolved method using *tert*-butyldimethyl((1-phenylcycloprop-2-en-1-yl)methoxy)silane **(42)** (65.1 mg, 0.25 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless oil in 60% yield (58.3 mg, 0.150 mmol). R_f : 0.47; dr: 92:8; er: 80:20; $[\alpha]_D^{20}$ -4.71 (c = 0.233, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.41 – 7.35 (m, 2H), 7.26 – 7.21 (m, 2H), 7.19 – 7.14 (m, 1H), 3.85 (d, J = 10.5 Hz, 1H), 3.74 (d, J = 10.4 Hz, 1H), 1.29 (s, 6H),

1.27 (s, 6H), 1.10 – 1.06 (m, 1H), 1.04 (dd, $J = 7.1, 3.7$ Hz, 1H), 0.77 (s, 9H), 0.39 (dd, $J = 9.2, 7.2$ Hz, 1H), -0.25 (s, 3H), -0.27 (s, 3H); ^{13}C (126 MHz, CDCl_3): δ 145.0, 130.3 (+, 2C), 127.7 (+, 2C), 126.3 (+), 83.3 (2C), 68.7 (-), 35.4, 26.1 (+, 3C), 25.2 (+, 2C), 24.8 (+, 2C), 18.5, 16.4 (-), 6.1, -5.5 (+), -5.6 (+); FTIR (KBr, cm^{-1}): 3059, 2978, 2955, 2928, 2885, 2856, 1472, 1416, 1379, 1321, 1252, 1213, 1146, 1088, 1076, 837, 773, 700; HRMS (TOF ES): Found 411.2523, calculated for $\text{C}_{22}\text{H}_{37}\text{BO}_3\text{SiNa}$ ($\text{M}+\text{Na}$) 411.2503 (4.9 ppm).

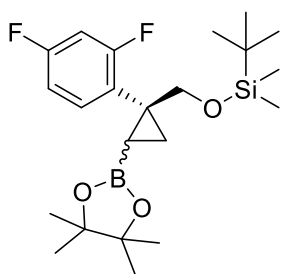


***tert*-butyl(((1*S*,2*R*)-1-(2,3-difluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methoxy)dimethylsilane (**63**)**

Compound was obtained via typical procedure for dissolved method using *tert*-butyl((1-(2,3-difluorophenyl)cycloprop-2-en-1-yl)methoxy)dimethylsilane (**60**) (148.0 mg, 0.50 mmol, 1.0 equiv.) and

allowing reaction to stir overnight. The product was purified by column chromatography using 20:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless oil in 72% yield (152.2 mg, 0.358 mmol). R_f 0.35; dr: 2.5:1; er: **Major (d1)**: 82:18 (Column IB, IPA 0.4%, Flow Rate 1.0mL/min) **Minor (d2)**: 73:27 (Column IB, IPA 0.4%, Flow Rate 1.0mL/min); $[\alpha]_{\text{D}}^{20}$ **Major (d1)**: -30.69 ($C = 1.88$, CHCl_3) **Minor (d2)**: -14.77 ($C = 0.88$, CHCl_3); ^{19}F NMR (376 MHz, CDCl_3) **Major (d1)**: δ -140.0 (d, $J = 20.8$ Hz), -141.2 (d, $J = 20.5$ Hz). **Minor (d2)**: δ -140.3 (d, $J = 21.0$ Hz), -140.5 (d, $J = 20.8$ Hz); ^1H NMR (500 MHz, CDCl_3): **Major (d1)**: δ 7.16 – 7.07 (m, 1H), 7.04 – 6.89 (m, 2H), 3.88 (d, $J = 10.7$ Hz, 1H), 3.71 (d, $J = 10.7$ Hz, 1H), 1.28 (s, 6H), 1.26 (s, 6H), 1.11 – 1.09 (m, 1H), 1.09 – 1.07 (m, 1H), 0.75 (s, 9H), 0.35 (t, $J = 8.4$ Hz, 1H), -0.23 (s, 3H), -0.27 (s, 3H). **Minor (d2)**: δ 7.10 – 7.04 (m, 1H), 7.04 – 6.91 (m, 2H), 3.86 (d, $J = 10.1$ Hz, 1H), 3.44 (d, $J = 10.2$ Hz, 1H), 1.16 (dd, $J = 9.6, 3.7$ Hz, 1H), 1.11 – 1.09 (m, 1H), 1.10 (s, 6H), 0.96 (s, 6H), 0.80 (s, 9H), 0.48 (dd, $J = 9.6, 7.0$ Hz, 1H), -0.10 (s, 3H), -0.14 (s, 3H); ^{13}C (126 MHz, CDCl_3): **Major (d1)**:

δ 150.6 (dd, J = 247.0, 12.8 Hz), 150.2 (dd, J = 248.6, 12.3 Hz), 134.2 (d, J = 10.8 Hz), 128.2 (+, t, J = 3.1 Hz), 123.0 (+, dd, J = 7.2, 4.6 Hz), 115.4 (+, d, J = 17.2 Hz), 83.4 (2C), 67.4 (-), 30.4 (d, J = 2.7 Hz), 26.0 (+, 3C), 25.2 (+, 2C), 24.7 (+, 2C), 18.4, 15.8 (-), 5.6 (+), -5.6 (+), -5.7 (+). **Minor (d2)**: δ 151.7 (dd, J = 249.5, 13.8 Hz), 151.6 (dd, J = 249.5, 16.4 Hz), 131.6 (d, J = 10.1 Hz), 128.1 (+, t, J = 3.2 Hz), 123.2 (+, dd, J = 6.6, 4.9 Hz), 115.3 (+, d, J = 16.8 Hz), 83.0 (2C), 68.9 (-), 29.8, 25.9 (+, 3C), 24.9 (+, 2C), 24.5 (+, 2C), 18.4, 14.4 (-), 4.1 (+), -5.5 (+), -5.5 (+); FTIR (KBr, cm⁻¹): 2978, 2956, 2929, 2885, 2857, 1372, 1324, 1255, 1213, 1146, 1090, 836, 780, 729; HRMS (TOF ES): Found 421.2893, calculated for C₂₄H₄₀BF₂OSi (M+H) 421.2910 (4.0 ppm).



***tert*-butyl(((1*S*,2*R*)-1-(2,4-difluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)methoxy)dimethylsilane (64)**

Compound was obtained via typical procedure for dissolved method using *tert* butyl((1-(2,4-difluorophenyl)cycloprop-2-en-1-yl)methoxy)dimethylsilane (**61**) (148.0 mg, 0.50 mmol, 1.0 equiv.) and allowing reaction to stir overnight. The product was purified by column chromatography using 20:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a clear oil in 79% yield (167.2 mg, 0.394 mmol). R_f : 0.30; dr: 2:1; er: **Major (d1)**: 82:18 (Column IB, IPA 0.2%, Flow Rate 1.0mL/min) **Minor (d2)**: 81:19 (Column IB, IPA 0.4%, Flow Rate 1.0mL/min); $[\alpha]_D^{20}$ **Major (d1)**: -31.08 (C = 2.04, CHCl₃) **Minor (d2)**: -18.89 (C = 1.44, CHCl₃); ¹⁹F NMR (376 MHz, CDCl₃) **Major (d1)**: δ -111.8 (d, J = 7.4 Hz), -113.0 (d, J = 6.9 Hz). **Minor (d2)**: δ -111.0 (d, J = 7.5 Hz), -113.3 (d, J = 7.3 Hz); ¹H NMR (500 MHz, CDCl₃): **Major (d1)**: δ 7.35 – 7.28 (m, 1H), 6.77 – 6.67 (m, 2H), 3.84 (d, J = 10.6 Hz, 1H), 3.66 (d, J = 10.6 Hz, 1H), 1.28 (s, 6H), 1.26 (s, 6H), 1.11 – 1.02 (m, 2H), 0.75 (s, 9H), 0.30 (dd, J = 9.2, 7.4 Hz, 1H), -0.24 (s, 3H), -0.27 (s, 3H). **Minor (d2)**: δ 7.32 – 7.21 (m, 1H), 6.81 – 6.73

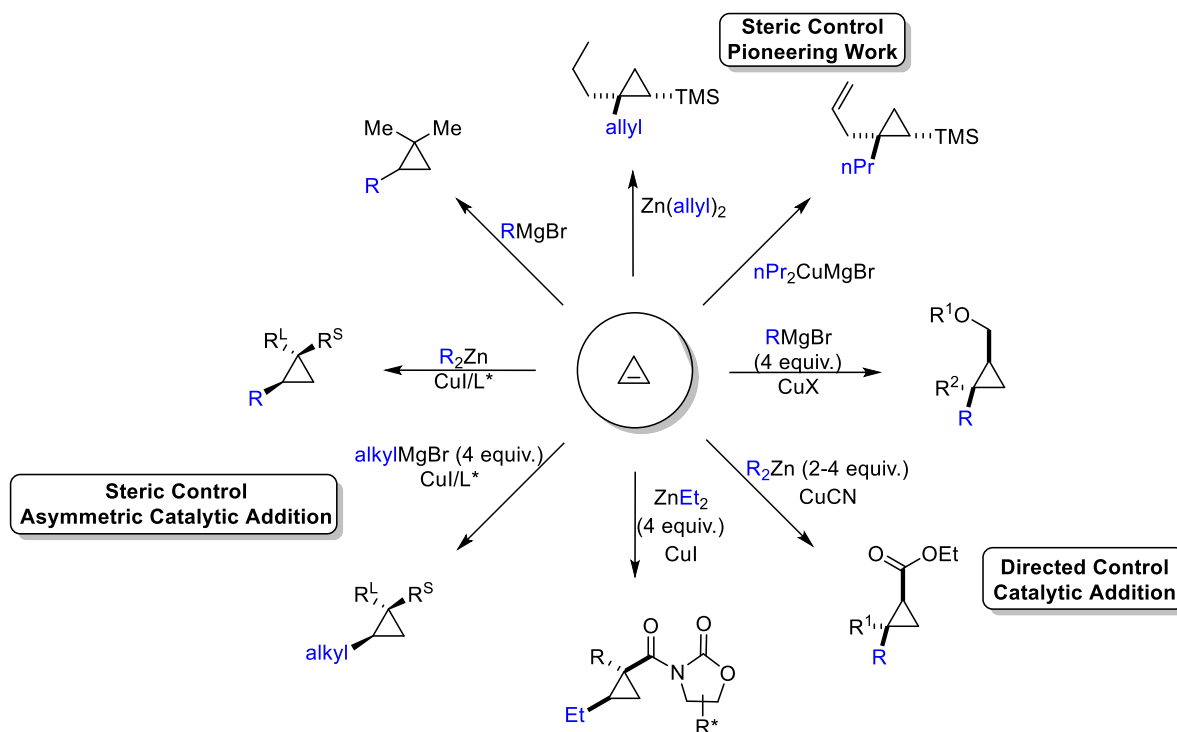
(m, 1H), 6.74 – 6.64 (m, 1H), 3.83 (d, $J = 10.1$ Hz, 1H), 3.39 (d, $J = 10.1$ Hz, 1H), 1.13 (dd, $J = 9.5$, 3.7 Hz, 1H), 1.10 (s, 6H), 1.07 (dd, $J = 7.1$, 3.7 Hz, 1H), 0.96 (s, 6H), 0.79 (s, 9H), 0.43 (dd, $J = 9.6$, 7.0 Hz, 1H), -0.11 (s, 3H), -0.15 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): **Major (d1)**: δ 163.0 (dd, $J = 249.5$, 12.6 Hz), 162.9 (dd, $J = 248.2$, 12.5 Hz), 134.4 (+, dd, $J = 9.5$, 5.9 Hz), 127.7 (dd, $J = 13.6$, 3.6 Hz), 110.3 (+, dd, $J = 20.8$, 3.6 Hz), 103.3 (+, t, $J = 25.5$ Hz), 83.4 (2C), 67.4 (-), 30.1, 26.0 (+, 3C), 25.2 (+, 2C), 24.7 (+, 2C), 18.4, 15.9 (-), 5.5 (+), -5.5 (+), -5.7 (+). **Minor (d2)**: δ 162.6 (dd, $J = 249.2$, 12.0 Hz), 162.0 (dd, $J = 246.5$, 12.0 Hz), 134.2 (+, dd, $J = 9.8$, 6.3 Hz), 125.0 (dd, $J = 13.7$, 3.6 Hz), 110.4 (+, dd, $J = 20.6$, 3.3 Hz), 103.3 (+, t, $J = 25.5$ Hz), 83.0 (2C), 69.1 (-), 29.4, 25.9 (+, 3C), 24.9 (+, 2C), 24.6 (+, 2C), 18.4, 14.4 (-), 4.1 (+), -5.5 (+), -5.5 (+); FTIR (KBr, cm^{-1}): 2979, 2952, 2929, 2887, 2858, 1598, 1504, 1446, 1415, 1371, 1359, 1325, 1257, 1083, 968, 837, 775; HRMS (TOF ES): Found 447.2299, calculated for $\text{C}_{22}\text{H}_{35}\text{BF}_2\text{O}_3\text{SiNa}$ ($\text{M}+\text{Na}$) 447.2314 (3.4 ppm).

Chapter 3. Directed Copper(I)-Catalyzed Carbomagnesiation of Cyclopropenes

3.1 Introduction

Carbometalation reactions involving the addition of organometallic reagents across the double bond of cyclopropene are among the most interesting transformations performed on the strained three-membered ring due to the potential of constructing carbon-carbon bonds in a stereoselective manner.^[41] Direct addition of Grignard,^[42] organozinc,^[43] and organocopper^[43] reagents under steric control have been known for more than 30 years. Recently, the catalytic delivery of such reagents has been developed. These reactions include copper-catalyzed asymmetric addition of organozinc^[44] and alkyl Grignard^[45] reagents to cyclopropenes in which diastereoselectivity is under steric control (**Scheme 29**). Additionally, the catalytic directed addition of Grignard^[46-48] and organozinc^[48] reagents has started to gain significant attention.

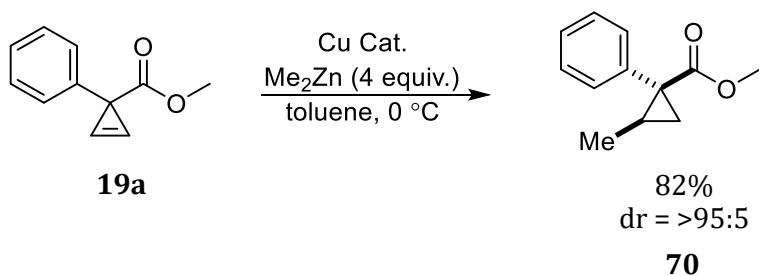
Scheme 29



Various directing groups including an alcohol,^[46] ether,^[47] ester,^[48] and an oxazolidinone^[48] auxiliary have been used to successfully direct carbomagnesiation to one face of cyclopropene. In 2016, an amide was shown by Marek to direct carbomagnesiation in a ring-opening process toward γ -ketoamides.^[49] However these methods generally require a large excess of organometallic reagent, extreme cooling, and suffer from poor diastereoselectivity and functional group tolerance. Furthermore, the addition of Grignard reagents in the presence of a carbonyl functionality remains a distinct challenge and thus has been limited to more docile organozinc reagents.

Fox^[48a] has previously developed a copper-catalyzed addition of organozinc reagents to 1-phenylcycloprop-2-ene-1-carboxylate. In this protocol, species **19a** underwent highly diastereoselective carbozincation in the presence of four equivalents of dimethylzinc at 0 °C. A subsequent protic quench provided cyclopropane **70** in 82% yield and >95:5 diastereomeric ratio (**Scheme 30**).

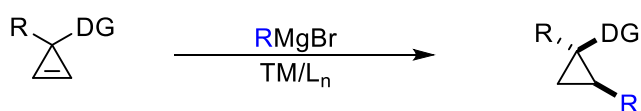
Scheme 30



The development of a protocol utilizing more reactive Grignard reagents would have several immediate advantages. Organozinc reagents are severely limited in availability with only dimethylzinc, diethylzinc, and diphenylzinc being commercially available. In order to utilize more exotic organozinc reagents, their in-situ synthesis from corresponding organolithium or Grignard

reagents is required. The development of a protocol utilizing more reactive Grignard reagents would not only vastly expand structural diversity but would also eliminate an entire labor intensive synthetic step. Therefore, we sought to develop a directed stereoselective catalytic addition of Grignard reagents to our recently developed cyclopropenylcarboxamide scaffolds for the synthesis of densely functionalized cyclopropanes (**Scheme 31**).

Scheme 31

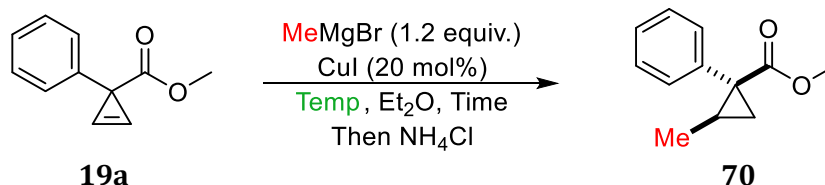


3.2 Early Reaction Screening

Initial attempts to achieve directed catalytic addition of Grignard reagents to cyclopropenes were conducted using cyclopropenylcarboxylate **19a**. This allowed for the direct benchmarking of the envisioned reaction against diastereoselective carbozincation as developed by Fox.^[51a] Experiments carried out at room temperature and at 0 °C showed that nearly all starting material decomposed into a complex mixture of products (**Table 18, entries 1, 2**). At -60 °C no reaction occurred but at -35 °C 72% yield was achieved with a 2:1 diastereomeric ratio (**entries 3, 4**). However, these results were a bit disappointing compared to the reaction with organozinc which provided far superior efficiency and diastereoselectivity (**Table 18, entry 5**). From here, attention was given to cyclopropene-3-carboxamides developed in chapter II, due to the general nature of amides as being less electrophilic and more Lewis basic as well as being less stabilizing of anions when compared to esters. Using amides could potentially provide several advantages over esters including allowing for elevated reaction temperatures, improved coordination to the catalyst, better configurational stability, and a greatly reduced propensity toward ring cleavage.

Delightfully, evaluation of diethylamide **53aa** under the best conditions for esters provided **71a** in excellent diastereoselectivity but in only 25% yield (**Scheme 32**).

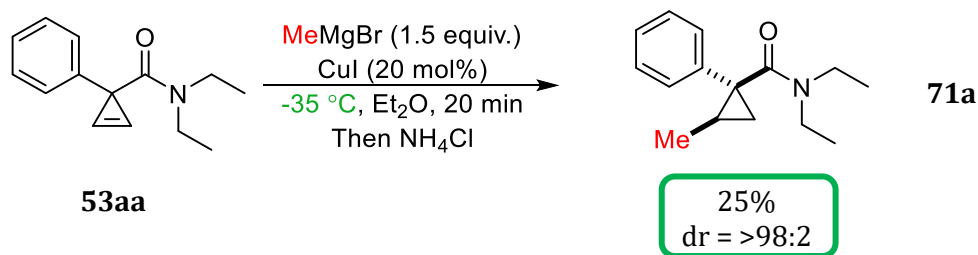
Table 18. Screening of ester directed Cu-catalyzed carbomagnesiation.



Entry	Temperature, °C	Time, h	dr ^[a]	Yield ^[b]
1	20	1	-	Decomposition
2	0	0.5	-	Trace
3	-60	4	-	No Conversion
4	-35	0.3	2:1	72%
5	Reaction with Organozinc^[48a]	0.3	>95:5	82%

[a] Determined by NMR of crude reaction mixture. [b] Isolated yield of purified product.

Scheme 32



3.3 Optimization of Grignard Reagent Addition to Cyclopropenenyamides

The high degree of facial selectivity observed in carbomagnesiation of **53aa** first prompted optimization toward improved chemical yield. Initially, an extension of reaction time to one hour was able to provide up to 76% yield (**Table 19, entry 2**). Any further increase in reaction time

had negligible effect on the reaction. Increasing the amount of Grignard reagent to two equivalents further increased yield to 89% (**entry 4**). Interestingly, a large excess of highly reactive methylmagnesium bromide did not have any detrimental effects on reaction efficiency (**entries 4, 5**). It was found that the catalyst loading could be greatly reduced, first to 10 mol% and even 5 mol% without any noticeable decline in chemical yield. However, a further decrease of catalyst loading below 5 mol% resulted in a sharp decline of yield (**entries 6-8**). Without catalyst the reaction was found to be inoperable and only provided trace evidence of any addition products (**entry 9**). A survey of ethereal solvents showed that yield correlated with the coordination ability of the solvent. Dimethoxyethane provided **71a** in near quantitative yield as essentially a single diastereomer (**entry 12**). Evaluation of several other fourth row transition metals was also conducted (**entries 13-19**). Marginal reactivity was found with iron(II) (**entry 16**) and cobalt(II) (**entry 17**) while no reactivity was observed with titanium(IV), vanadium(IV), manganese(II), or nickel(II) (**entries 13 - 15, 18**). However, neither iron(II) or cobalt(II) was remotely comparable to the efficiency demonstrated with both copper(I) and copper(II) salts (**entries 12, 19**). The trend in copper salt reactivity ($\text{CuI} > \text{CuCN} > \text{CuBr} > \text{CuCl}$) correlated with the solubility of these species in DME (**entries 12, 20 - 22**). The reaction with carboxamide **53aa** was found to be operable at room temperature but still resulted in considerable formation of over addition products (**entry 23**). Slight cooling to 0 °C using a simple ice water bath was found to be the optimal reaction temperature, providing **71a** as a single diastereomer in 97% yield (**entry 24**). At this temperature the reaction was surprisingly fast and reached full conversion and 96% yield in under five minutes (**entries 25-27**). Finally, the amount of Grignard reagent was able to be reduced to as low as 1.35 equivalents while still obtaining the monoaddition product **71a** as a single diastereomer in near quantitative yields (**Table 19, entry 28**)!

Table 19. Optimization of amide directed catalytic carbomagnesiation.

53aa $\xrightarrow[\text{Then NH}_4\text{Cl}]{\text{MeMgBr Catalyst, Temp, Solvent, Time}}$ 71a

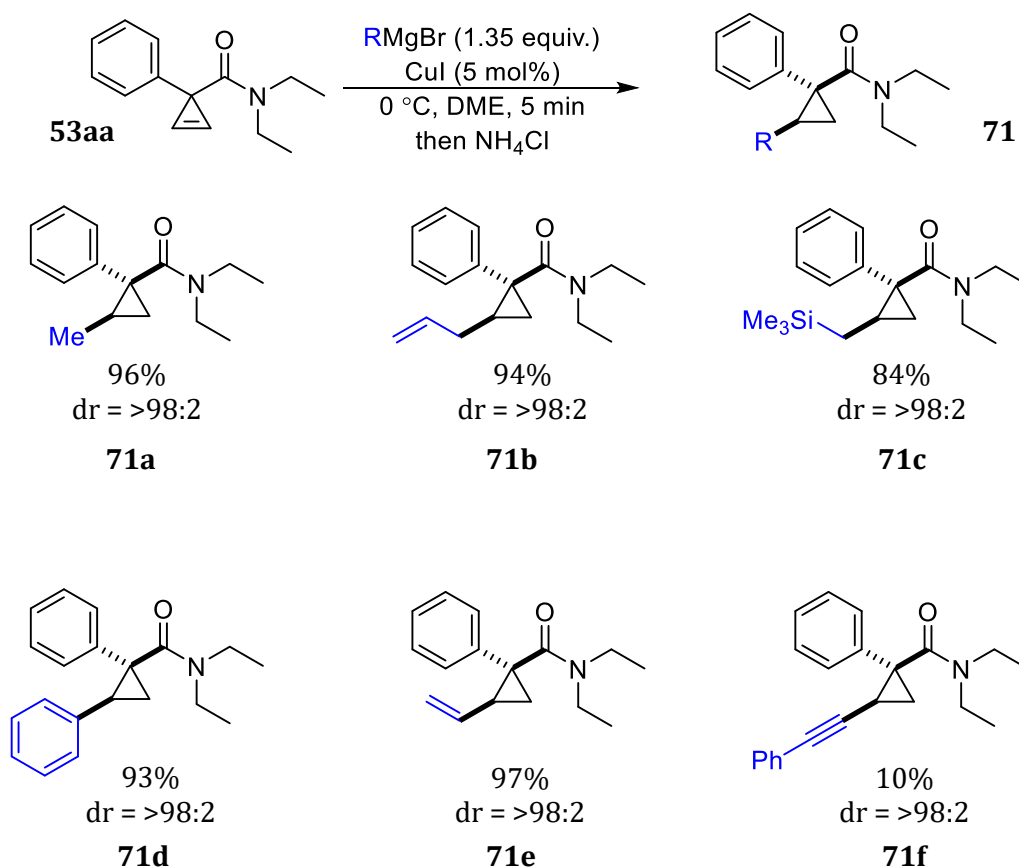
Entry	Cat. (mol%)	MeMgBr (equiv.)	Solvent (4 mL)	Temp (°C)	Time (min)	Yield ^[a] (%)	dr ^[b]
1	CuI (20)	1.5	Et ₂ O	-35	30	25	>98:2
2	CuI (20)	1.5	Et ₂ O	-35	60	76	>98:2
3	CuI (20)	1.5	Et ₂ O	-35	120	78	>98:2
4	CuI (20)	2.0	Et ₂ O	-35	60	89	>98:2
5	CuI (20)	3.0	Et ₂ O	-35	60	87	>98:2
6	CuI (10)	2.0	Et ₂ O	-35	60	89	>98:2
7	CuI (5)	2.0	Et ₂ O	-35	60	86	>98:2
8	CuI (2.5)	2.0	Et ₂ O	-35	60	63	>98:2
9	None	2.0	Et ₂ O	-35	60	<2	-
10	CuI (5)	2.0	MTBE	-35	60	13	>98:2
11	CuI (5)	2.0	THF	-35	60	90	>98:2
12	CuI (5)	2.0	DME	-35	60	99	>98:2
13	Ti(Cp) ₂ Cl ₂ (10)	2.0	DME	-35	60	<2	-
14	V(O)(AcAc) ₂ (10)	2.0	DME	-35	60	<2	-
15	MnCl ₂ (10)	2.0	DME	-35	60	<2	-
16	FeBr ₂ (10)	2.0	DME	-35	60	40	>98:2
17	CoCl ₂ (10)	2.0	DME	-35	60	36	>98:2
18	NiCl ₂ (10)	2.0	DME	-35	60	<2	-
19	CuCl ₂ (10)	2.0	DME	-35	60	98	>98:2
20	CuCN (5)	2.0	DME	-35	60	74	>98:2
21	CuBr (5)	2.0	DME	-35	60	64	>98:2
22	CuCl (5)	2.0	DME	-35	60	13	>98:2
23	CuI (5)	2.0	DME	20	60	58	>98:2
24	CuI (5)	2.0	DME	0	60	97	>98:2
25	CuI (5)	2.0	DME	0	30	96	>98:2
26	CuI (5)	2.0	DME	0	15	94	>98:2
27	CuI (5)	2.0	DME	0	5	96	>98:2
28	CuI (5)	1.35	DME	0	5	95	>98:2

[a] NMR yield of crude reaction mixtures with dibromomethane as standard. [b] Determined by NMR of crude reaction mixture, >98:2 indicates minor diastereomer was not observed by ¹H NMR.

3.4 Evaluation of Grignard Reagent Scope

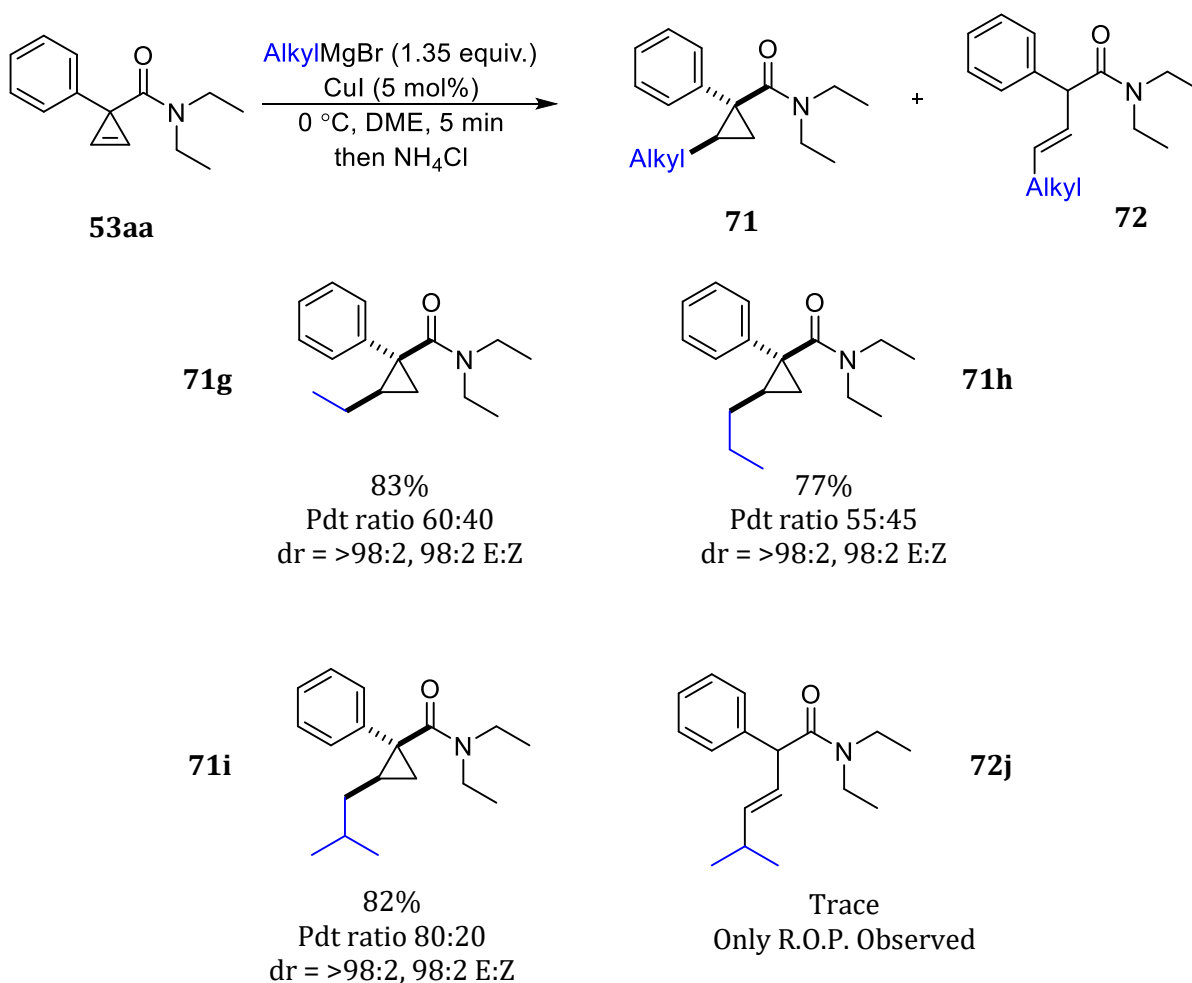
Next, a variety of other Grignard reagents were evaluated using the conditions optimized for the delivery of methylmagnesium bromide (**Table 20**). The reaction proved to be extremely diastereoselective and high yielding with methyl **71a**, allyl **71b**, and (trimethylsilyl)methyl **71c** Grignard reagents. sp^2 -Hybridized phenyl and vinyl Grignard reagents were also efficient nucleophiles and provided **71d** and **71e** very efficiently. Even the less nucleophilic sp -hybridized acetylenic reagent **71f** also provided high diastereoselectivity.

Table 20. Evaluation of Grignard reagent scope.



Interestingly, when extended alkyl Grignard reagents were used, the reaction became much more complex and resulted in a mixture of ring-retentive and ring-opened products **71** and **72** (Table 21). This intriguing observation does not offer an immediate rationale based on traditional steric and electronic factors and invokes consideration of more subtle London dispersion effects,^[45, 51] the complex and variable aggregate supramolecular structures^[52] of cuprates in solution, and solvent effects influencing cation Lewis acidity and the Schlenk equilibrium. Isopropylmagnesium bromide proved to be too sterically demanding and resulted in only traces of the ring opened product (R.O.P) **72j**.

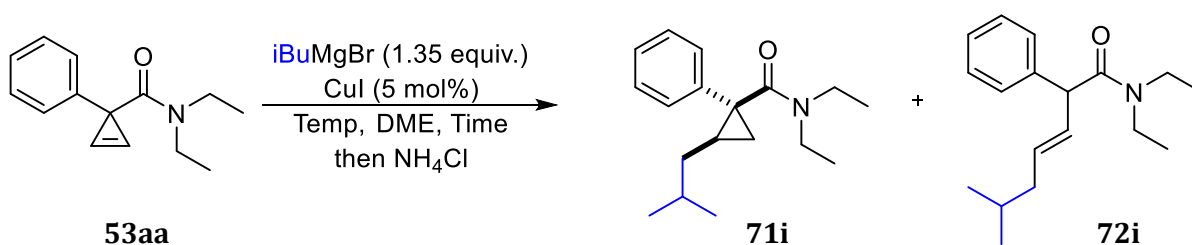
Table 21. Evaluation of alkyl Grignard reagent scope.



3.5 Optimization and Evaluation of Addition of Alkyl Grignard Reagents

Optimization of the addition of isobutylmagnesium bromide to cyclopropene **53aa** was conducted (**Table 22**). It became immediately apparent that cooling the reaction to -78 °C shutdown the reaction while only slight cooling using a brine/ice bath still resulted in considerable amounts of ring-opened product **72i** (**Table 22, entries 1, 2**). Conducting the reaction at -35 °C and -45 °C for 90 minutes only slightly increased the product ratio. It was found that stirring for 60 minutes at -45 °C provided full conversion in addition to suppressing ring opening (**entry 5**).

Table 22. Optimization of catalytic carbomagnesiation involving alkyl Grignard reagents.



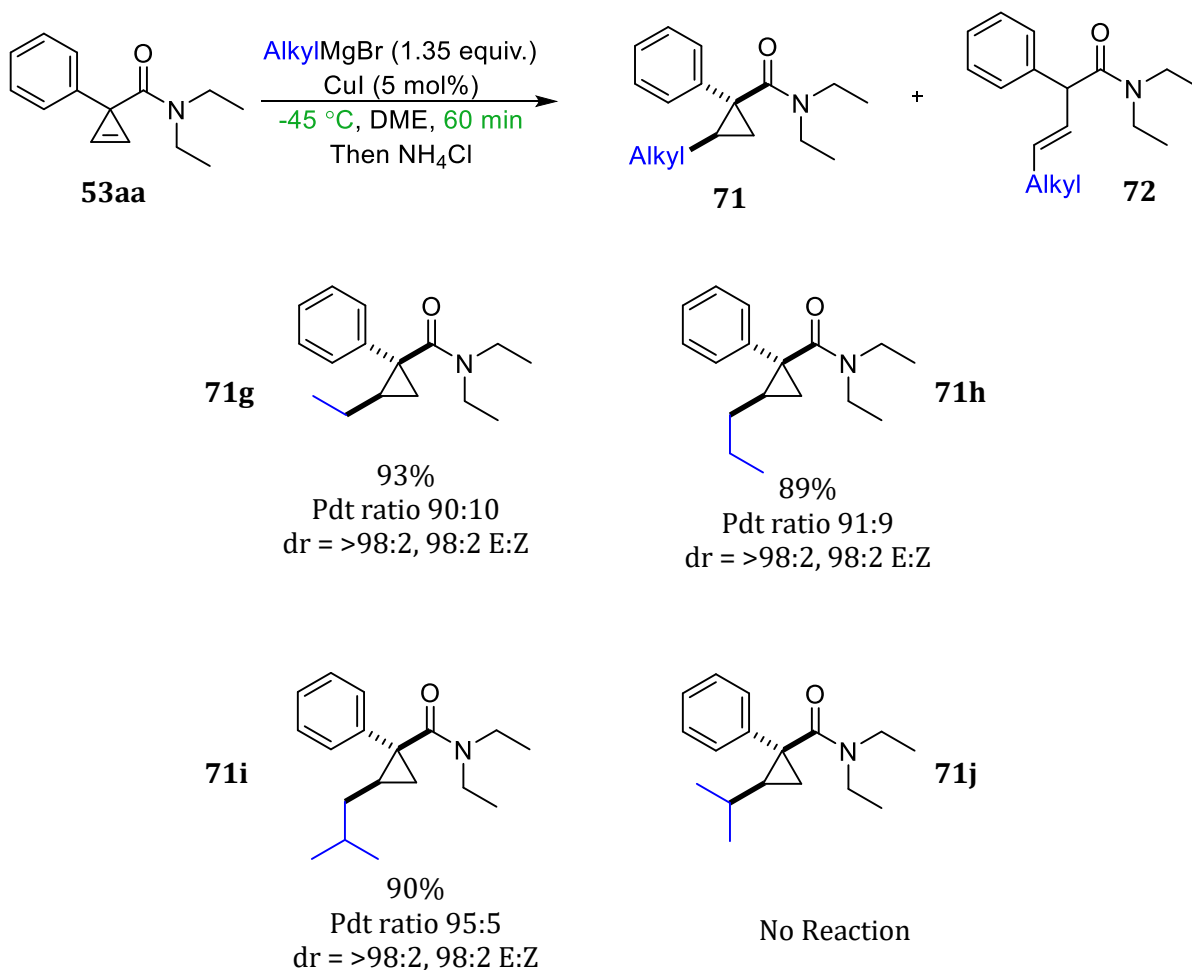
Entry	Temp (°C)	Time (min)	Yield (%) ^[a]	Pdt Ratio ^[b]
1	-78	60	5	>99:1
2	-10	15	80	89:11
3	-35	90	94	88:12
4	-45	90	91	91:9
5	-45	60	90	95:5

[a] NMR yield of crude reaction mixtures using dibromomethane as standard. [b] Determined by NMR of crude reactions.

Subjecting the problematic alkyl Grignard reagents to cyclopropene **53aa** at reduced temperature with prolonged reaction time allowed for the cyclopropane products **71g**, **71h**, and

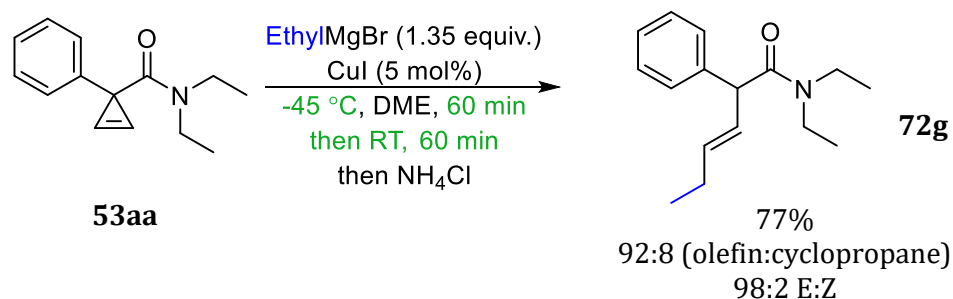
71i to be obtained as the major product in excellent yield (**Table 23**). Isopropylmagnesium bromide failed to show any reactivity under these altered conditions.

Table 23. Ring-retentive addition of alkyl Grignard reagents.



It was also possible to drive this process toward the ring opened product by first conducting the reaction at -45 °C for one hour and then allowing the reaction to warm to and stir for one hour at room temperature to provide **72g** as the *E*-configured olefin in 77% yield (**Scheme 33**).

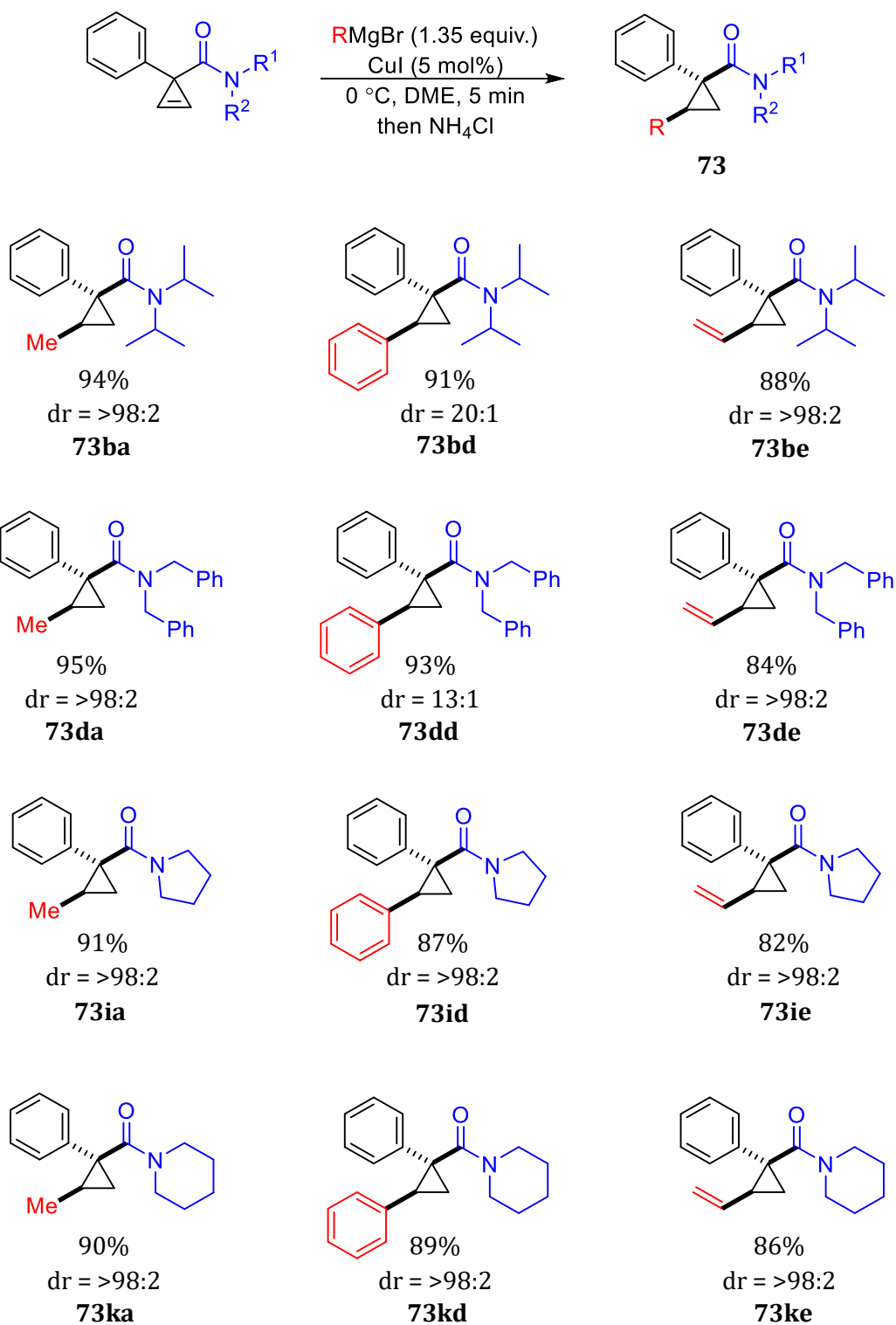
Scheme 33

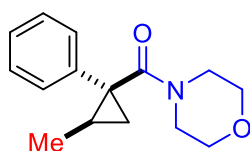


3.6 Evaluation of Amide Scope

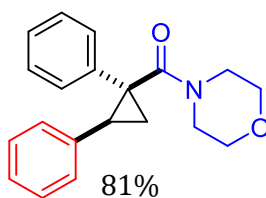
A wide variety of tertiary cyclopropene-3-carboxamides possessing various substituents on nitrogen were evaluated with methyl-, phenyl-, and vinylmagnesium bromide nucleophiles (**Table 24**). Generally, yields and diastereoselectivities were extremely high even with very sterically demanding diisopropylamides **73ba** and **73be**. Cyclic amides were compatible with all Grignard reagents, providing *cis*-configured cyclopropanes **73ia** – **73ke** in excellent yield and extremely high diastereoselectivity. In fact, the reactions were so efficient that the product obtained following extraction was of >95% purity and could be considered sufficiently pure for subsequent synthetic applications. The only reduction in diastereoselectivity was observed in the most sterically demanding combinations such as phenylmagnesium bromide with diisopropylamide **73bd** and dibenzylamide **73dd**.

Table 24. Evaluation of amide compatibility.

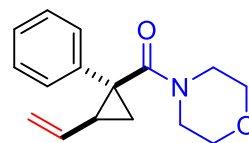




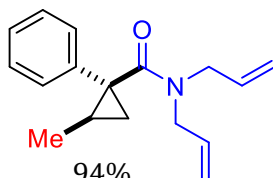
92%
dr = >98:2
73ja



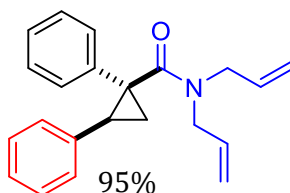
81%
dr = >98:2
73jd



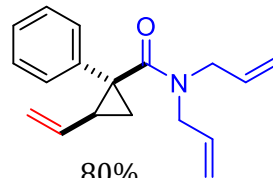
83%
dr = >98:2
73je



94%
dr = >98:2
73ca



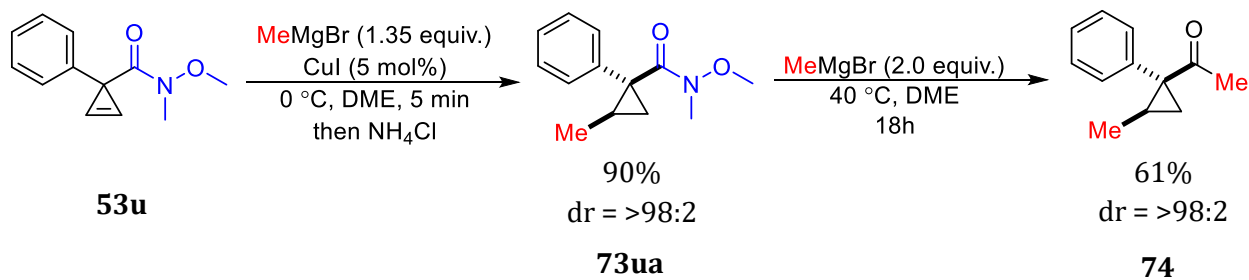
95%
dr = 9:1
73cd



80%
dr = >98:2
73ce

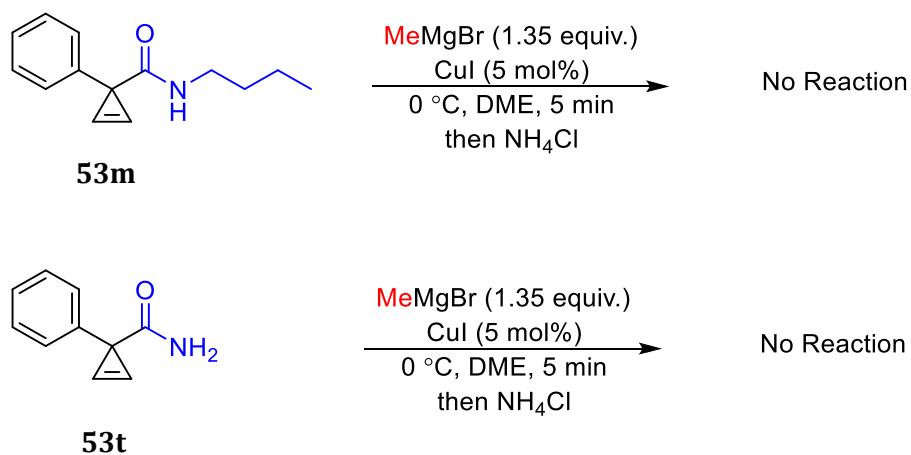
It was also possible to access cyclopropyl ketones via utilization of the Weinreb amide as a directing group (**Scheme 34**). Upon exposure to methylmagnesium bromide cyclopropene **53u** underwent efficient chemo- and diastereoselective carbometallation followed by a protic quench to provide **73ua** in excellent yield. Subsequent introduction of additional Grignard reagent combined with slightly elevated temperature allowed for the efficient conversion of the amide into the corresponding methyl ketone **74**.

Scheme 34



It is important to note that the amide directed copper(I)-catalyzed Grignard reagent addition reaction is strictly limited to the use of tertiary amides. All attempts to conduct carbomagnesiation involving secondary **53m** or primary **53t** amides failed to provide any reactivity and intact cyclopropene was recovered in both cases (**Scheme 35**). Most likely, initial deprotonation of the acidic N-H bond led to sequestration of the copper catalyst and resulted in a complete shutdown of reactivity. This follows with previous observations which require copper catalyst to activate the cyclopropene double bond toward addition. Attempts to increase Grignard reagent loading to correct for losses due to deprotonation still only returned starting material.

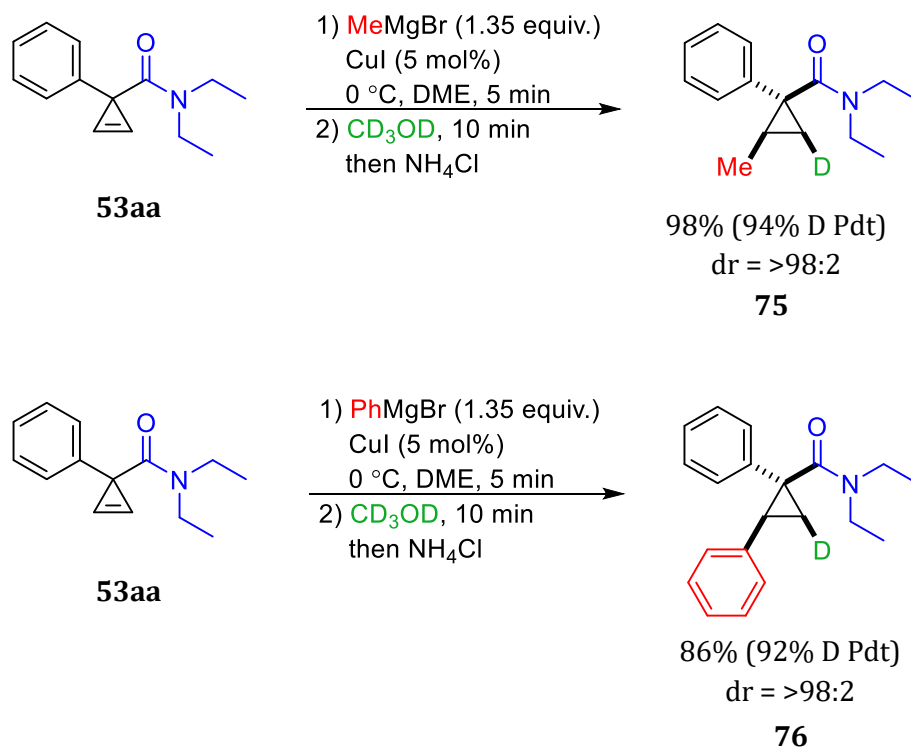
Scheme 35



3.7 Carbomagnesiation Followed by Non-Protic Quench

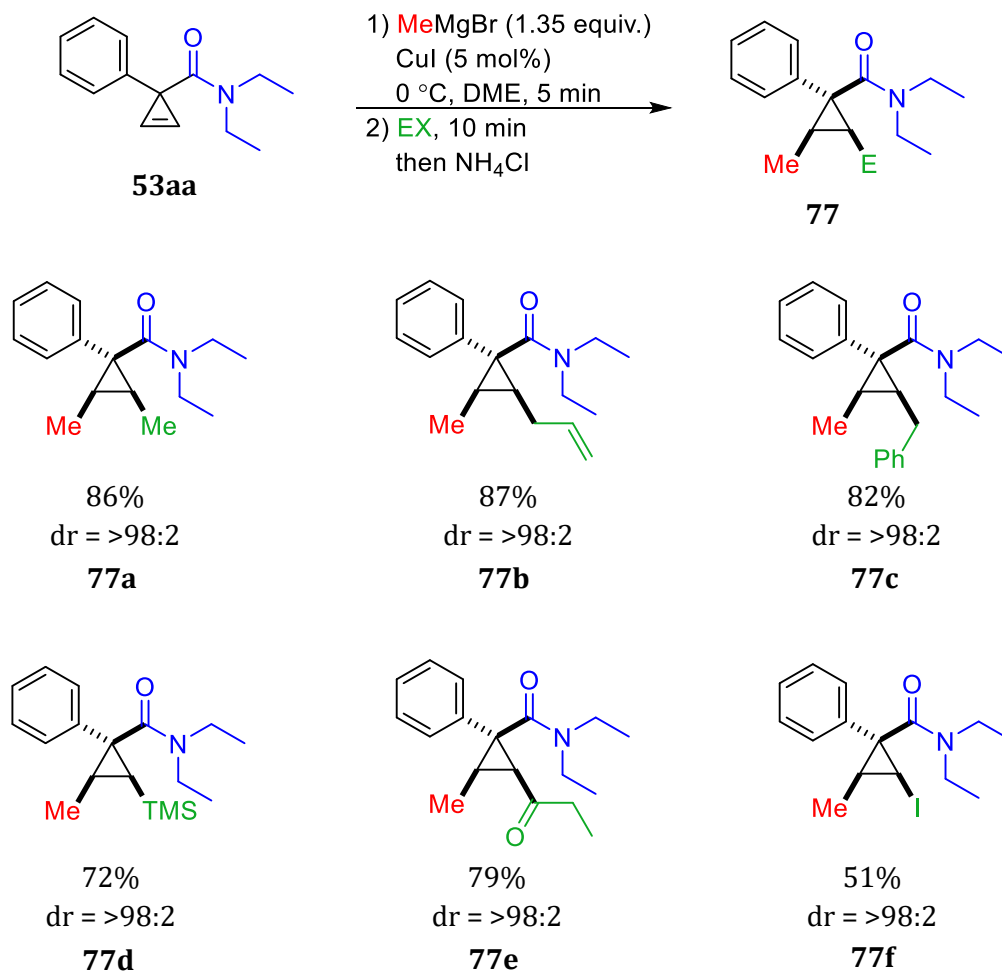
The possibility of incorporating additional electrophiles across the double bond of cyclopropene became of interest. With some optimization, it was found that the reaction could be quenched with methanol-*d* to provide deuterium labeled *cis*-configured cyclopropanes **75** and **76** in high yield (**Scheme 36**)

Scheme 36



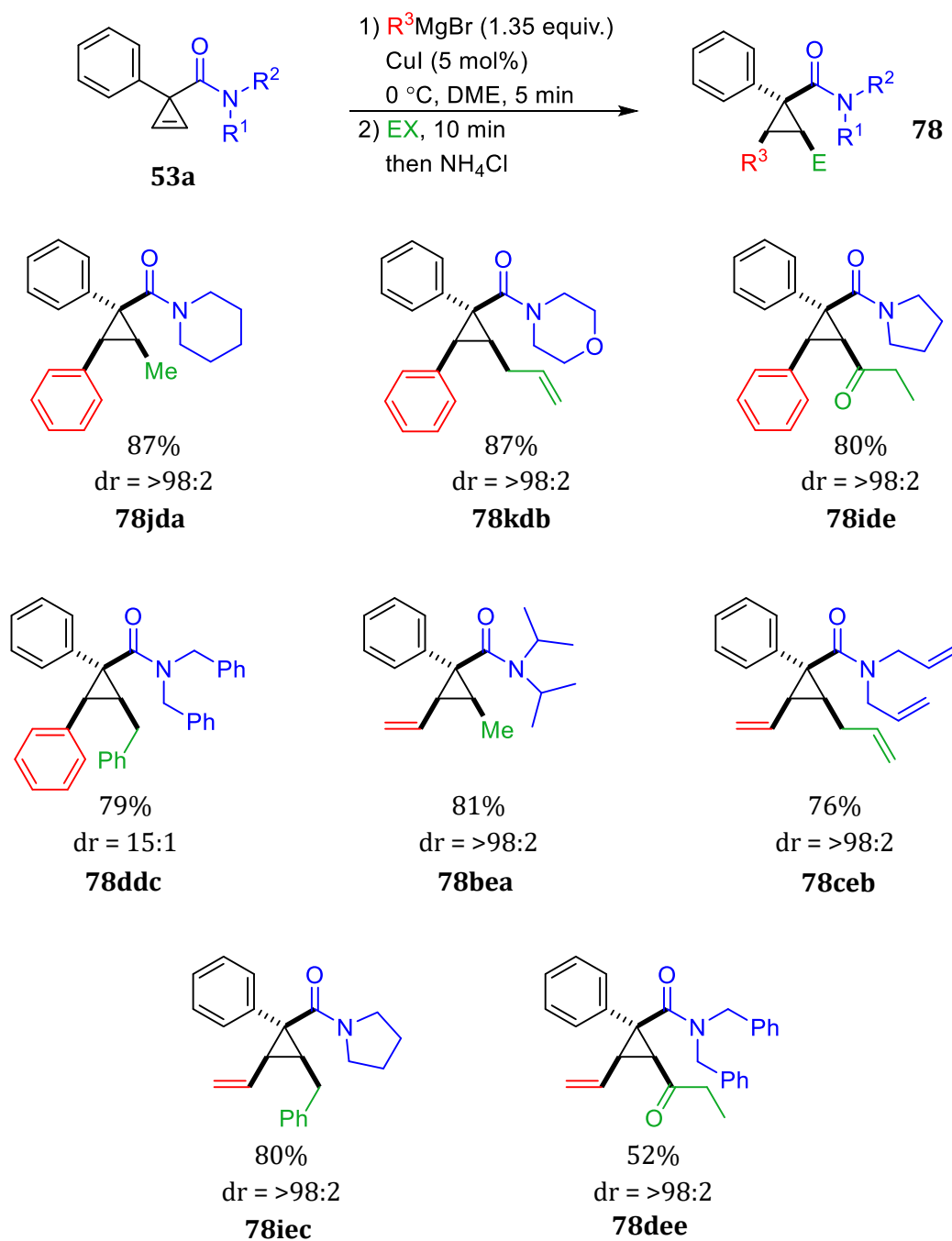
Next, this chemistry was extended to feature the variety of compatible electrophiles. It was found that quenching with S_N2-active alkyl halide electrophiles methyl iodide, allyl bromide, and benzyl bromide provided tetrasubstituted cyclopropanes **77a** – **77c** as single diastereomers in high yield (**Table 25**). Considerably more bulky TMSCl was found to be compatible with the reaction with MeMgBr as nucleophile to provide species **77d**. Attempts to incorporate this electrophile with more sterically encumbered phenyl- or vinylmagnesium bromide failed and the protonated compounds **71d** or **71e** were isolated from these reactions as the sole products. Interestingly, electrophilic trapping with freshly distilled propionyl chloride provided a highly efficient diastereoselective route to cyclopropyl ketone **77e** without any evidence of tertiary alcohol formation. Iodine was also successfully utilized as an electrophile to give stereodefined cyclopropyl iodide **77f**.

Table 25. Carbomagnesiation followed by incorporation of non-protic electrophiles.



Finally, a set of cyclopropanes exhibiting the vast variability compatible with this transformation were synthesized (**Table 26**). The only decline in diastereoselectivity across all examples exhibiting the carbomagnesiation/electrophilic trapping sequence, was observed in **78ddc** possessing excessively sterically demanding dibenzyl amide and phenylmagnesium bromide as the nucleophile. Several interesting examples include **78ceb** and **78dee** which are candidates for the formation of interesting ring systems via ring-closing metathesis and a strain-release driven rearrangement respectively.

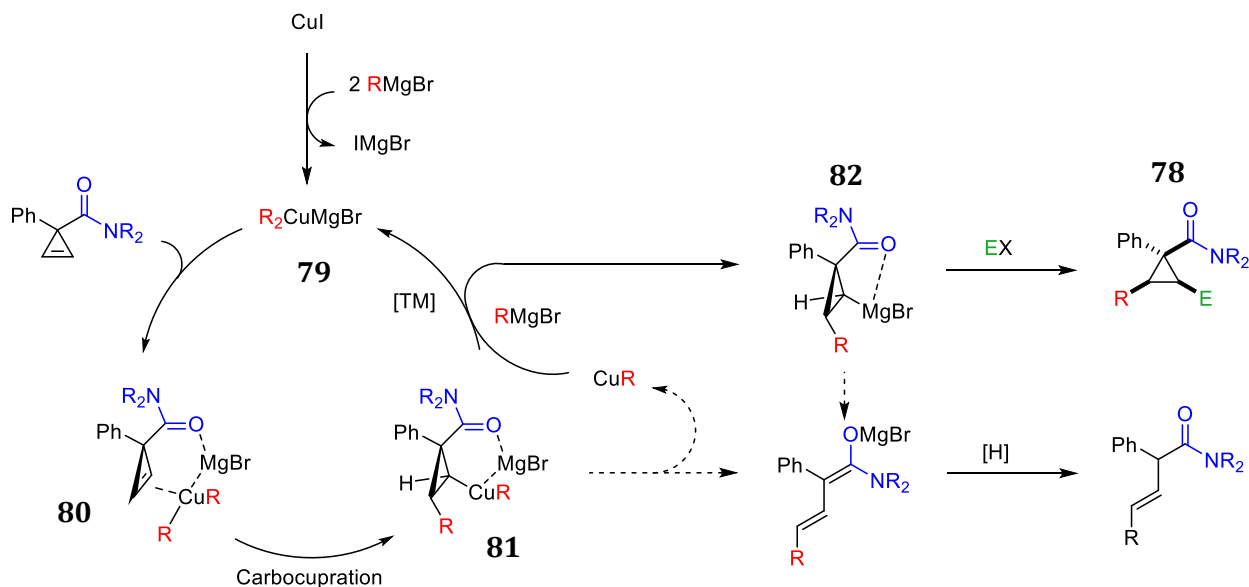
Table 26. Variation compatible with the carbomagnesiation/electrophilic trapping sequence.



3.8 Discussion of Mechanism

Based on experimental observations, a possible reaction pathway has been devised (**Scheme 37**). Initially, copper(I) iodide is converted to the corresponding Gilman-type cuprate **79** during a premixing period prior to the introduction of cyclopropene. Upon addition of cyclopropene, the cuprate complex is delivered to one face of cyclopropene via coordination with the amide function to establish species **80**. From here, copper is able to activate the double bond which then undergoes an overall carbocupration to provide cyclopropyl cuprate species **81**. Transmetallation returns the Gilman cuprate **79** to the catalytic cycle and generates a cyclopropyl Grignard reagent species **82**. Subsequent exposure of the cyclopropyl Grignard reagent to an electrophile results in the production of *cis*-configured cyclopropane **78** as a single diastereomer. Alternatively, systems experiencing significant destabilization of species **81** could undergo direct decomposition toward the ring-opened product. During this process, the released monoorganocuprate would be converted back to Gilman cuprate species **79** following transmetallation with another equivalent of Grignard reagent.^[53]

Scheme 37

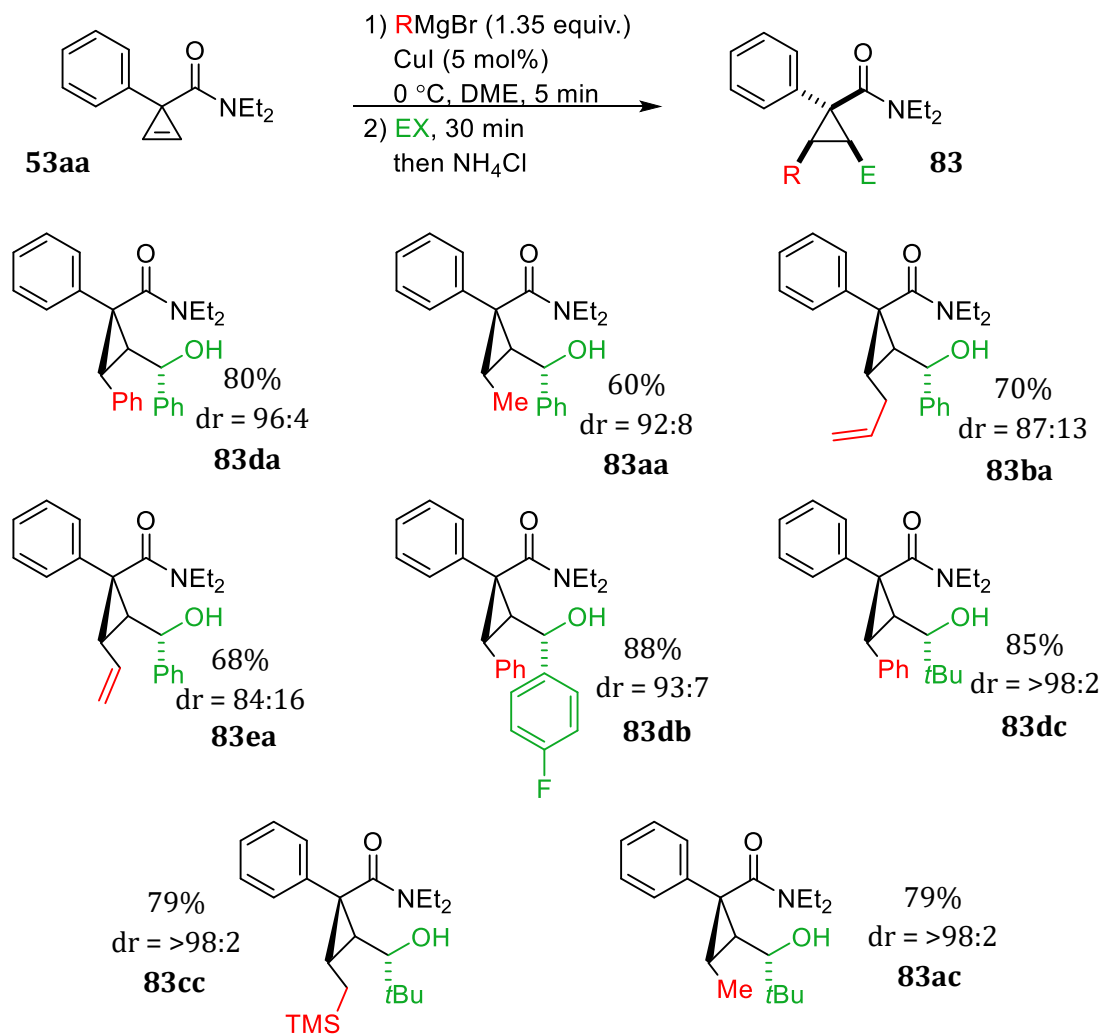


3.9 Carbomagnesiation Followed by Diastereoselective Quench with Prochiral

Electrophiles

Due to the apparent high conformational and configurational rigidity of the cyclopropyl Grignard reagent species **82**, the possibility of conducting a diastereoselective addition to prochiral electrophiles was considered. By extending the reaction time following introduction of an aldehyde, the production of products possessing four contiguous stereocenters was possible (Table 27).

Table 27. Carbomagnesiation followed by diastereoselective quench with prochiral electrophiles.

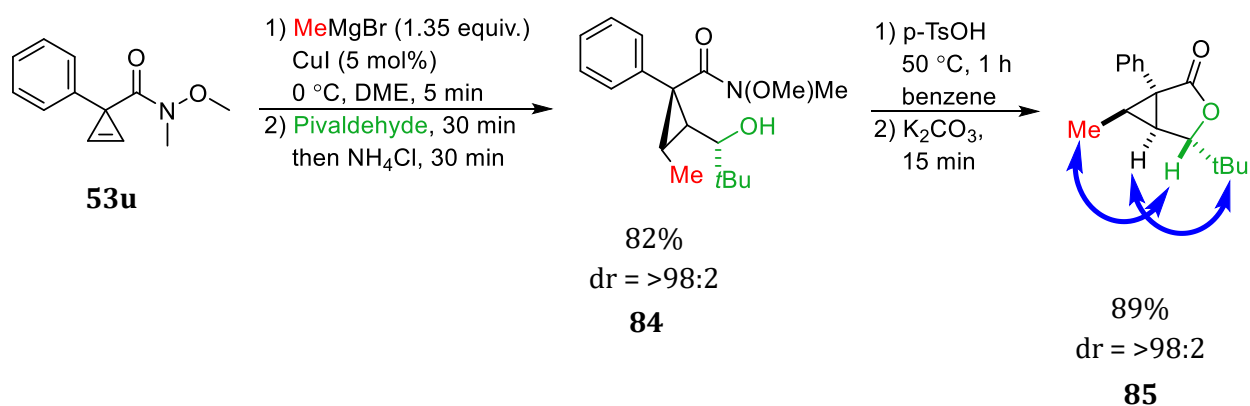


In a series of reactions with different Grignard reagents all quenched by benzaldehyde, diastereoselectivity generally declined with diminishing steric influence of the nucleophilic component moving from phenyl substituted **83da** to vinyl substituted **83ea**. Furthermore, diastereoselectivity could be greatly increased when very sterically demanding pivaldehyde was used which provided products **83dc**, **83cc**, and **83ac** as a single diastereomer in all combinations of Grignard reagents.

3.10 Determination of Relative Stereochemistry

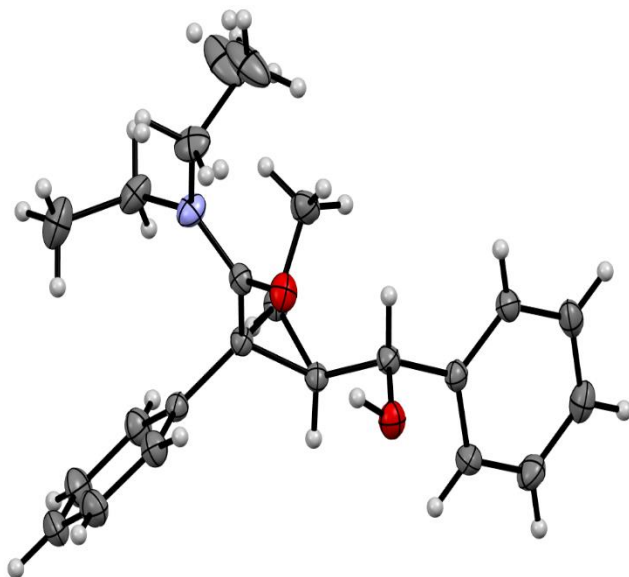
The relative stereochemistry of the cyclopropylmethanol products in **Table 27** was first confirmed by NMR methods using Weinreb amide **53u**, which underwent efficient carbomagnesiation followed by quenching with pivaldehyde to provide **84** (**Scheme 38**). Exposure of **84** to acidic conditions resulted in the formation of the corresponding fused lactone **85**. NOESY NMR analysis showed very strong methyl/H(green) and *tert*-butyl/H(black) correlations thus providing strong evidence for the *cis-trans*-configured product.^[50]

Scheme 38



X-ray analysis of structure **83aa**, provided confirmation of the stereochemical outcome of the carbomagnesiation/electrophilic trapping sequence (**Figure 6**). It can clearly be seen that carbomagnesiation occurs across the same face of cyclopropene without inversion of the intermediate cyclopropylmagnesium bromide **82** as the amide, methyl nucleophile, and aldehyde electrophile are all located on the same face of cyclopropane. Furthermore, orientation of the hydroxyl group toward the amide, as it would be in lactone, places the two phenyl rings on the convex face of the molecule as predicted in structure **85**.

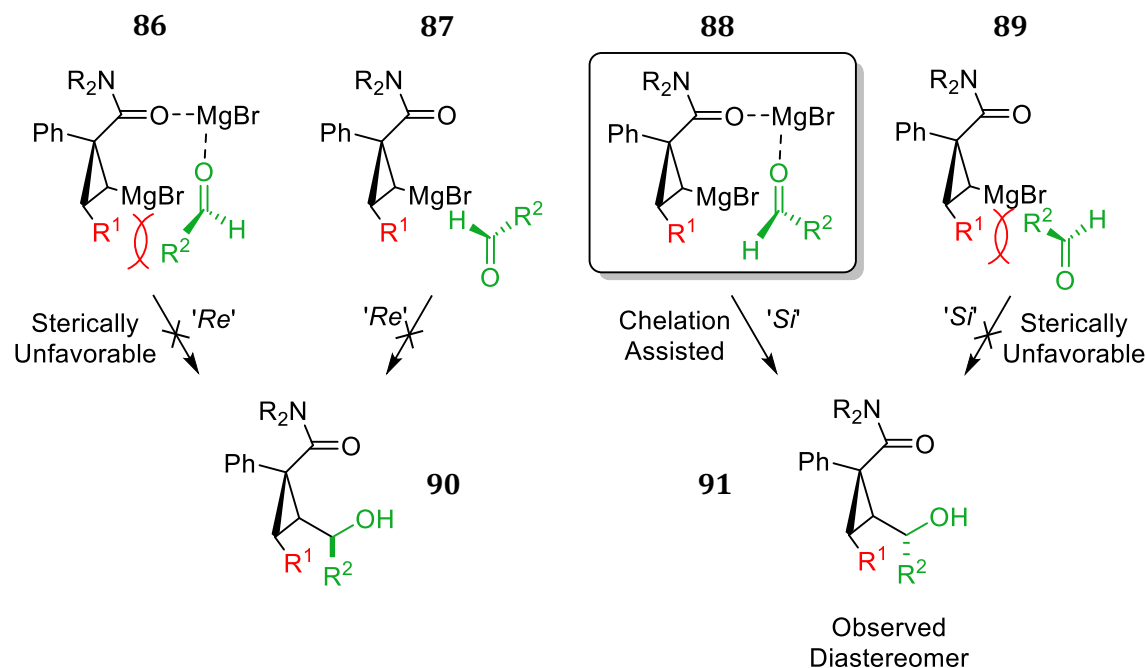
Figure 6. ORTEP drawing of **83aa** showing 50% probability amplitude displacement ellipsoids.



The highly diastereoselective formation of products **83** was rationalized via conformational analysis of proposed complexes **86** - **89** (**Scheme 39**). Structures **86** and **89** can be considered highly unfavorable due to the significant steric interaction expected between R¹ of cyclopropane and R² of the aldehyde. Complexes **87** and **88**, providing diastereomeric products **90** and **91** respectively, would be expected to experience relatively similar steric interactions. Therefore,

the highly diastereoselective formation of product **91** can likely be attributed to a stabilizing chelation-control effect resulting in selective addition of cyclopropylmagnesium bromide to the '*S*' face of the aldehyde.

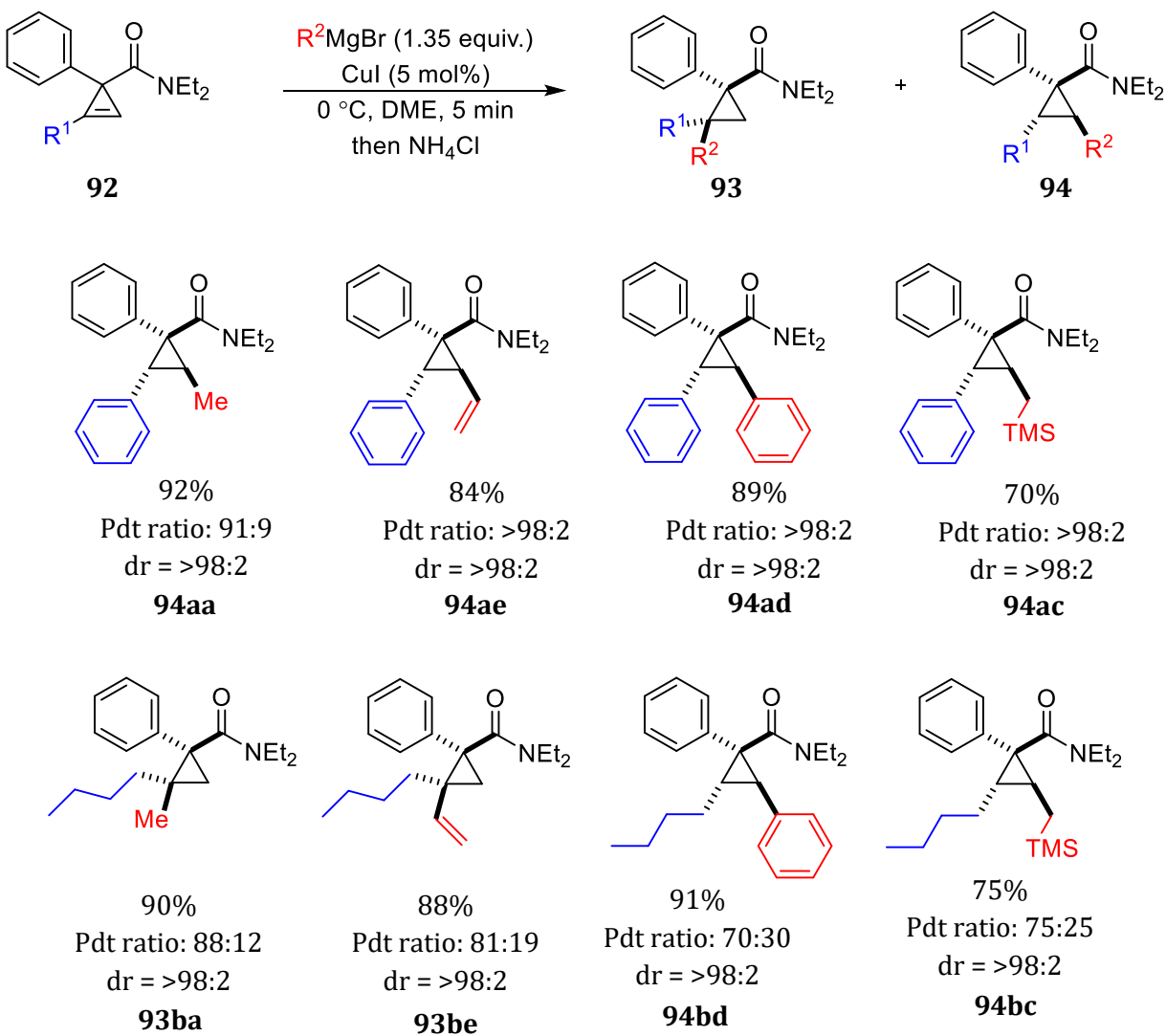
Scheme 39



3.11 Carbomagnesiation with Substituted Cyclopropenes

Finally, the regioselectivity of carbomagnesiation on a substituted double bond of cyclopropene was investigated (**Table 28**). With phenyl substituted cyclopropenes high selectivity for vicinally substituted products **94aa** – **94ae** was observed. However, when a butyl substituent was placed on cyclopropene the selectivity becomes more variable. Methyl and vinyl nucleophiles provided selectivity toward germinal products **93ba** and **93be**, while phenyl and (trimethylsilyl)methyl selectively formed vicinally substituted products **94bd** and **94bc**. In all cases, yields were high and products were obtained as single diastereomers.

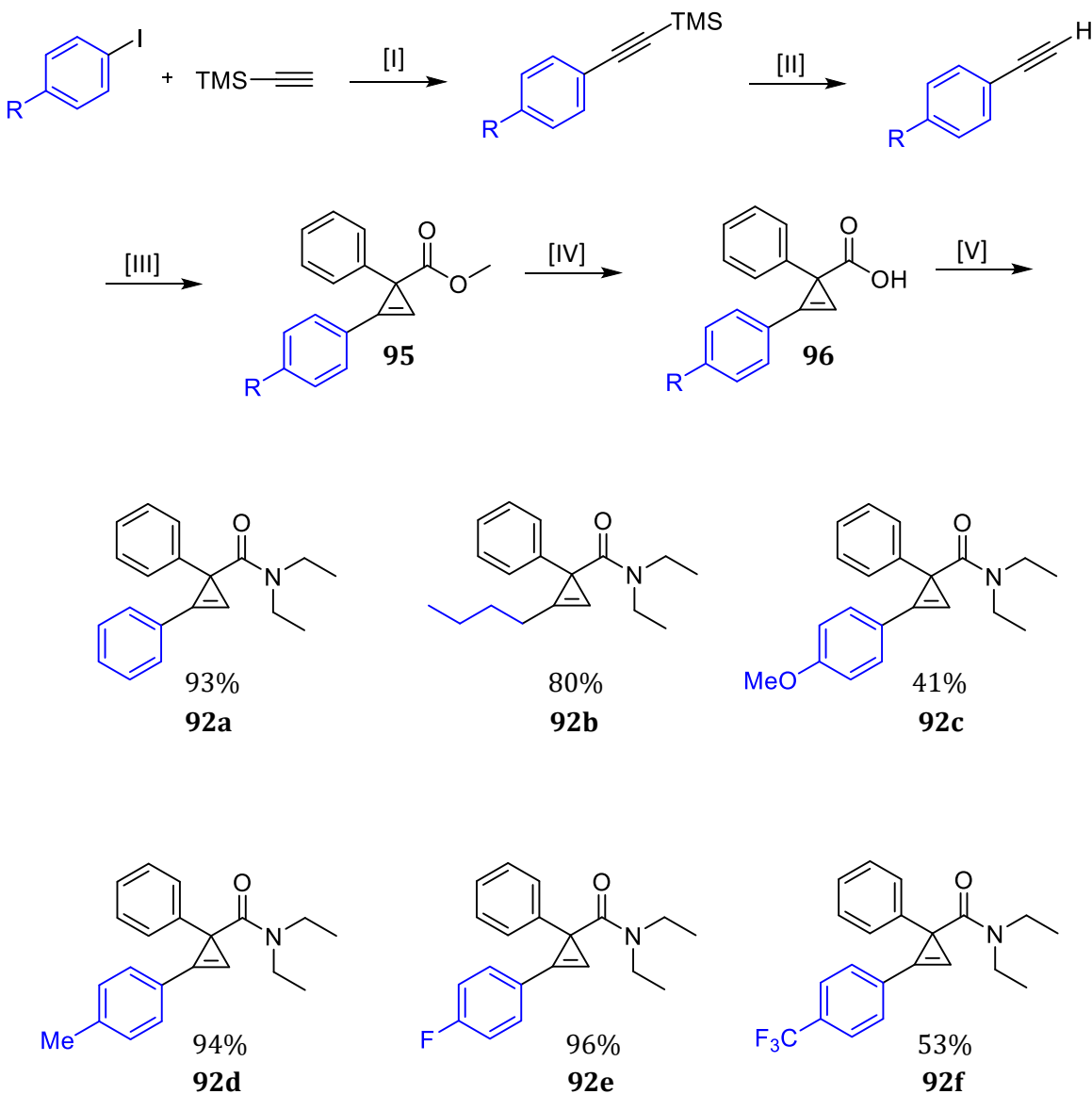
Table 28. Regioselectivity of carbomagnesiation on substituted cyclopropene double bond.



To probe electronic influences on the carbomagnesiation reaction, a series of phenyl-substituted cyclopropenes bearing groups of varying electronics in the 4-position were evaluated (**Table 30**). These cyclopropenes were accessed via Sonogashira coupling of the corresponding aryl halide with TMS-acetylene followed by desilylation. Cyclopropanation with methyl phenyldiazoacetate then provided substituted cyclopropenylcarboxylates **95**, which could be

readily hydrolyzed under basic conditions to carboxylic acid species **96**. A peptide coupling sequence then provided *p*-substituted aryl cyclopropenes **92a** – **92f** (Table 29).

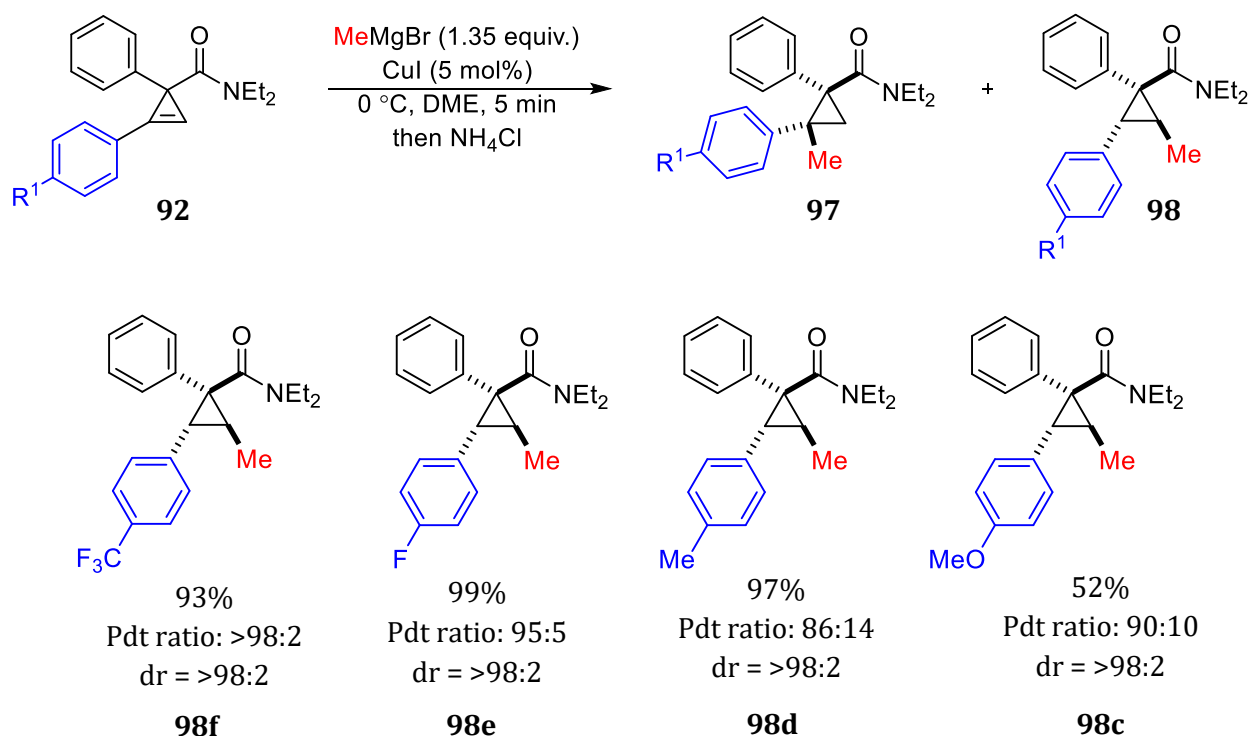
Table 29. Synthesis of phenyl-substituted cyclopropenes of varying electronics.



[I] $\text{Pd}(\text{PPh}_3)_4$, CuI , NEt_3 , THF; [II] K_2CO_3 , THF:MeOH (1:1); [III] $\text{Rh}_2(\text{OAc})_4$, methyl phenyldiazoacetate; [IV] NaOH , MeOH/THF (1:1); [V] $(\text{COCl})_2$, NEt_3 , HNEt_2 or DCC, HOBT, HNEt_2 . See Experimental for specific detail.

Substrates bearing electron withdrawing substituents in the para-position of the phenyl ring displayed the highest efficiency and selectivity with **98f** being obtained exclusively as the vicinal product as a single diastereomer. Evaluation of substrate **98c** which possessed an electron-donating *p*-methoxy substituent resulted in greatly diminished yield and slightly deteriorated regioselectivity. Generally, regioselectivity increased with increasingly electron deficient cyclopropenes (**Table 30**).

Table 30. Electronic influence on carbomagnesiation.



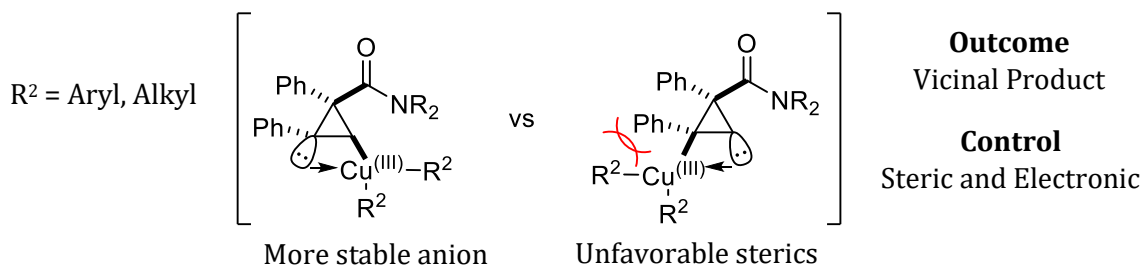
The regioselectivity of products **94** and **98** was rationalized by evaluation of the intermediate cyclopropylcopper(III) complexes in **Figure 7**. These structures are believed to form following addition of the nucleophilic Gilman cuprate to the electrophilic double bond of cyclopropene during a carbocupration sequence. The equilibrium between the two interconverting

regioisomers is proposed to directly influence the subsequent regiodefining C-C bond forming reductive elimination to cyclopropylcuprate species **81**.

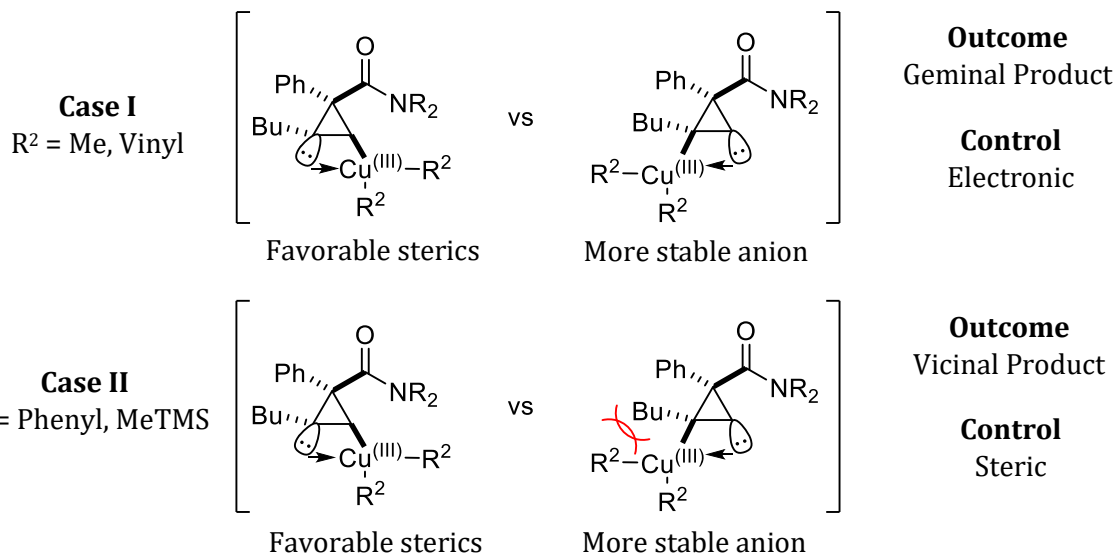
With phenyl-substituted cyclopropenes, the combined influence of the more stable anionic intermediate, also experiencing minimal steric interactions, led to the highly selective formation of vicinally substituted products **94aa–94ae** (**Figure 7a**). Reactions involving butyl-substituted cyclopropenes resulted in mixtures of products in all examples due to competing steric and electronic influences. These reactions are also highly dependent on the steric signature of the cuprate (**Figure 7b**). In case I, when R^2 is a relatively small methyl or vinyl group, steric interactions are minimal therefore allowing the reactions to proceed under electronic control via the formation of the most stable anionic intermediate to provide geminally substituted products **93ba** and **93be**. In case II, when R^2 is a more sterically demanding phenyl or (trimethylsilyl)methyl group, the reactions are governed by steric control and provide vicinally substituted products **94bd** and **94bc**. The trend in regioselectivity observed in phenyl-substituted cyclopropenes in **Table 30** can solely be attributed to the electronic influences of the substituent in the 4-position of the phenyl ring upon the anionic cyclopropylcopper(III) intermediate (**Figure 7c**). A highly electron-withdrawing *p*-CF₃ substituent provided further electronic stabilization to the anion and provided vicinally substituted **98f** as the sole product. Exchanging the substituent for electron-donating *p*-methoxy destabilized the anionic intermediate and resulted in the deteriorated regioselectivity observed in substrate **98c**.

Figure 7. Model for carbomagnesiation regioselectivity.

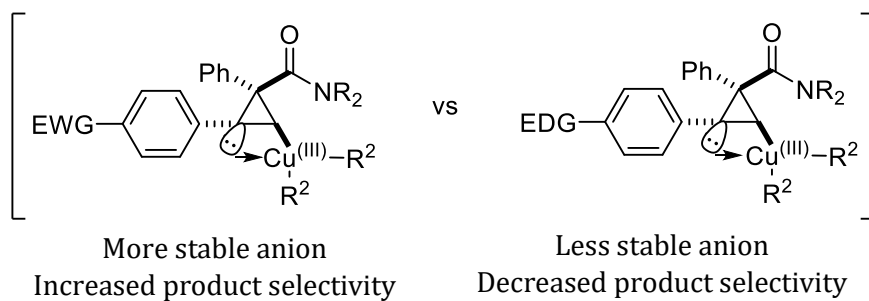
a)



b)

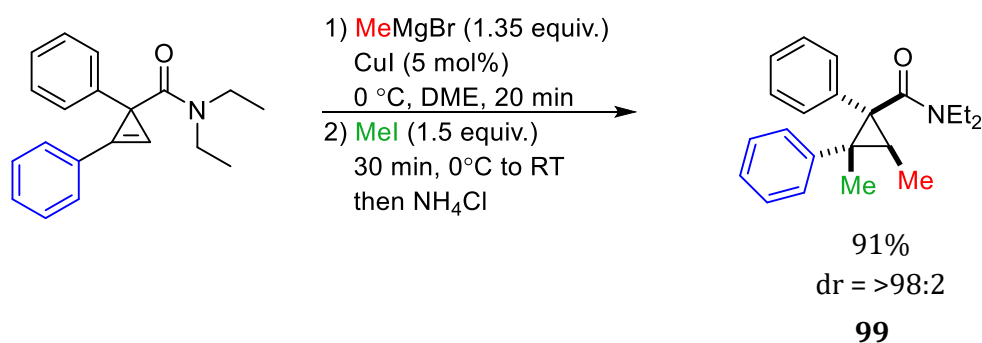


c)



Lastly, the ability to apply the developed carbomagnesiation/electrophilic trapping reaction toward the synthesis of stereodefined cyclopropanes possessing two quaternary stereocenters was successfully demonstrated (**Scheme 40**). Sterically congested penta-substituted cyclopropane **99** was obtained in excellent yield and diastereoselectivity.

Scheme 40

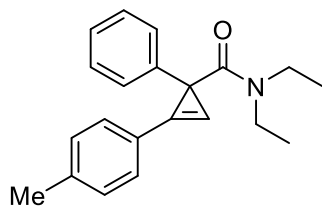


3.12 Conclusion

In conclusion, the directed copper(I)-catalyzed addition of Grignard reagents across the strained double bond of cyclopropenes has been developed. The high degree of conformational and configurational stability of the intermediate cyclopropyl Grignard reagent has allowed for the highly diastereoselective trapping with a variety of electrophiles, including prochiral aldehydes providing for the construction of two carbon-carbon bonds and four contiguous stereocenters in a single chemical step. Finally the developed methodology was evaluated on substituted cyclopropenes and was found to be extremely regio- and diastereoselective with electron deficient double bonds and could even be further extended to the synthesis of penta-substituted cyclopropanes bearing two quaternary stereocenters in a highly efficient and diastereoselective manner.

3.13 Experimental

3.13.1 Synthesis of Substituted Cyclopropene Amides

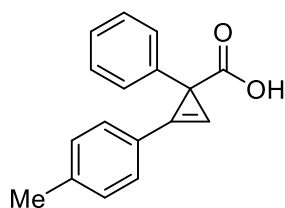


N,N-diethyl-1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxamide (92d)

[Typical Amide Procedure]: 1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxylic acid (**96d**) (250 mg, 1.0 mmol, 1.0 equiv.) and

dimethylformamide (2 drops) were dissolved in freshly distilled and dried dichloromethane (7 mL) and added to a flame dried round bottom flask under an inert nitrogen atmosphere. Oxalyl chloride (130 μ L, 190 mg, 1.5 mmol, 1.5 equiv.) was then added slowly dropwise and stirred at room temperature for 2 hours. The solution was then evaporated under reduced pressure to provide a pale yellow solid material. **Part 2:** diethylamine (206 μ L, 146 mg, 2.0 mmol, 2.0 equiv.) and triethylamine (280 μ L, 202 mg, 2.0 mmol, 2.0 equiv.), and freshly dried dichloromethane (6.0 mL) were combined in a flame dried two neck round bottom flask under an inert nitrogen atmosphere. Recovered material from part 1 was dissolved in freshly dried dichloromethane (6.0 mL) and added to the two neck flask slowly dropwise. The reaction was then stirred for 18 hours and then partitioned between water and dichloromethane. The aqueous phase was then acidified using 1N HCl to a pH of approximately 2. The organic phase was then extracted with properly acidified water (pH = 2, 3 x 10mL). The combined acidic aqueous layers were then back extracted once with dichloromethane which was combined with other organic layers, washed with brine, dried, filtered, and concentrated. The product was then purified by silica gel column chromatography using a 2:1 hexane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 94% yield (288 mg, 0.943 mmol). mp: 123.3 – 125.7 $^{\circ}$ C; R_f : 0.29; 1 H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.32 – 7.23 (m, 4H), 7.22 – 7.12 (m, 3H), 7.03 (s, 1H), 3.53

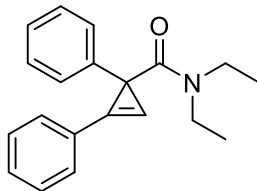
(dq, $J = 14.3, 7.1$ Hz, 2H), 3.31 (dq, $J = 14.0, 7.1$ Hz, 2H), 2.33 (s, 3H), 1.19 (t, $J = 7.1$ Hz, 3H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 173.3, 142.9, 139.9, 130.4 (+, 2C), 129.4 (+, 2C), 128.4 (+, 2C), 126.2 (+), 126.1 (+, 2C), 123.5, 122.1, 97.8 (+), 42.2 (-), 39.0 (-), 35.4, 21.7 (+), 13.8 (+), 12.7 (+); FTIR (KBr, cm^{-1}): 3081, 3023, 2972, 2933, 1625, 1457, 1275, 1118, 820, 700; HRMS (TOF ES): Found 328.1682, calculated for $\text{C}_{21}\text{H}_{23}\text{NONa}$ ($\text{M}+\text{Na}$) 328.1677 (1.5 ppm).



1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxylic acid (96d)

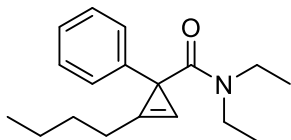
[Typical Hydrolysis Procedure]: A solution of methyl 1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxylate (**95d**) (300 mg, 1.13 mmol, 1.0 equiv.) in a 1:1 mixture of methanol:tetrahydrofuran (20 mL) was

stirred at 0 °C. A 1.5 M aqueous solution of sodium hydroxide (8 mL) was added dropwise and the mixture was stirred for 18 hours. Organic solvents were then removed under vacuum and the remaining aqueous solution was added to dichloromethane (20 mL). The mixture was acidified to pH 2 with 1N aqueous HCl. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic phases were washed with brine, dried with MgSO_4 , filtered, and concentrated. The obtained product is typically pure enough to be used in further amide coupling as is, however, if necessary, further purification can be achieved by column chromatography on silica gel using a 1:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as colorless solid in 92 % yield (261 mg, 1.04 mmol). mp: 134.5 – 135.9 °C; R_f : 0.19; ^1H NMR (500 MHz, CDCl_3) δ 7.56 – 7.51 (m, 2H), 7.45 – 7.39 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.18 (m, 3H), 7.13 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 181.3, 140.7, 140.4, 130.1 (+, 2C), 129.8 (+, 2C), 128.5 (+, 2C), 128.1 (+, 2C), 126.7 (+), 122.4, 116.7, 98.7 (+), 33.2, 21.7 (+); FTIR (KBr, cm^{-1}): 3137, 3025, 1684, 1408, 1224, 1173, 819, 698; HRMS (TOF ES): Found 251.1075, calculated for $\text{C}_{17}\text{H}_{15}\text{O}_2$ ($\text{M}+\text{H}$) 251.1072 (1.2 ppm).



N,N-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (92a)

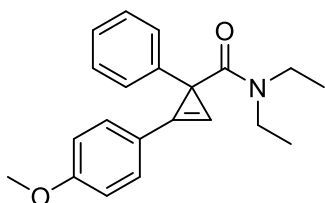
Compound was obtained via [typical amide procedure] using 1,2-diphenylcycloprop-2-ene-1-carboxylic acid (**96a**) (400 mg, 1.69 mmol, 1.0 equiv.). The product was then purified by silica gel column chromatography using a 1:1 hexane:ethyl acetate mobile phase to provide the titled compound as a golden oil in 93% yield (458 mg, 1.57 mmol). *R_f*: 0.53; ¹H NMR (500 MHz, CDCl₃): δ 7.89 – 7.71 (m, 2H), 7.41 – 7.29 (m, 7H), 7.23 – 7.18 (m, 1H), 7.14 (s, 1H), 3.72 – 3.47 (m, 2H), 3.41 – 3.26 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 3H); ¹³C (126 MHz, CDCl₃): δ 173.1, 142.6, 130.3 (+, 2C), 129.6 (+), 128.6 (+, 2C), 128.4 (+, 2C), 126.3, 126.2 (+), 126.0 (+, 2C), 122.3, 98.7 (+), 42.1 (-), 38.9 (-), 35.4, 13.7 (+), 12.6 (+); FTIR (KBr, cm⁻¹): 3080, 3059, 2974, 2933, 2873, 1682, 1614, 1445, 1427, 1381, 1277, 1221, 1072, 922, 768, 698, 644; HRMS (TOF ES): Found 292.1699, calculated for C₂₀H₂₂NO (M+H) 292.1701 (0.8 ppm).



2-butyl-N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (92b)

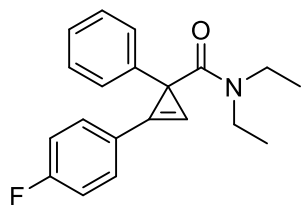
Compound was obtained via [typical amide procedure] using 2-butyl-1-phenylcycloprop-2-ene-1-carboxylic acid (**96b**) (450 mg, 2.08 mmol, 1.0 equiv.). The product was then purified by silica gel column chromatography using a 3:1 hexane:ethyl acetate mobile phase to provide the titled compound as a very pale yellow oil in 80% yield (434 mg, 1.60 mmol). *R_f*: 0.34; ¹H NMR (500 MHz, CDCl₃): δ 7.23 – 7.16 (m, 2H), 7.12 – 7.01 (m, 3H), 6.59 (s, 1H), 3.45 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.29 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.16 (dq, *J* = 14.4, 7.3 Hz, 2H), 2.63 – 2.45 (m, 2H), 1.59 – 1.42 (m, 2H), 1.35 – 1.18 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.79 (q, *J* = 7.1 Hz, 6H); ¹³C (126 MHz, CDCl₃): δ 174.1, 143.9, 128.3 (+ 2C), 125.9 (+, 2C), 125.8 (+), 124.2, 98.2 (+), 41.9

(-), 38.7 (-), 34.2, 29.2 (-), 24.2 (-), 22.4 (-), 13.8 (+), 13.6 (+), 12.7 (+); FTIR (KBr, cm^{-1}): 3082, 3057, 2961, 2932, 2972, 1643, 1634, 1614, 1493, 1445, 1423, 1379, 1275, 1221, 1099, 856, 700; HRMS (TOF ES): Found 272.2019, calculated for $\text{C}_{18}\text{H}_{26}\text{NO}$ ($\text{M}+\text{H}$) 272.2014 (1.8 ppm).



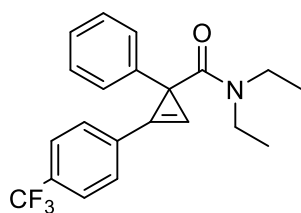
N,N-diethyl-2-(4-methoxyphenyl)-1-phenylcycloprop-2-ene-1-carboxamide (92c)

Trimethylamine (83 μL , 59.7 mg, 0.590 mmol, 1.5 equiv.) was added to 2-(4-methoxyphenyl)-1-phenylcycloprop-2-ene-1-carboxylic acid (**96c**) (105 mg, 0.390 mmol, 1.0 equiv.) dissolved in tetrahydrofuran (5 mL). The solution was then cooled to 0 $^{\circ}\text{C}$. *N,N'*-Dicyclohexylcarbodiimide (122 mg, 0.590 mmol, 1.5 equiv.), 1-Hydroxybenzotriazole hydrate (80.0 mg, 0.590 mmol, 1.5 equiv.), and diethylamine (52.0 μL , 37.3 mg, 0.51 mmol, 1.3 equiv.) were then added sequentially and the reaction was allowed to warm to room temperature over approximately 1 hour before being heated to 42 $^{\circ}\text{C}$ and stirred for 24 hours. Solvent was evaporated and the crude material was directly purified by silica gel column chromatography using a 3:1 hexane:ethyl acetate mobile phase to provide the titled product as a an amber oil in 41% yield (51.7 mg, 0.161 mmol). R_f : 0.26; ^1H NMR (500 MHz, CDCl_3) δ 7.70 (d, J = 8.7 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.23 (m, 2H), 7.20 – 7.14 (m, 1H), 6.94 (s, 1H), 6.87 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 3.53 (dq, J = 14.3, 7.1 Hz, 2H), 3.29 (dq, J = 14.0, 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 173.4, 160.9, 142.9, 132.1 (+, 2C), 128.5 (+, 2C), 126.2 (+), 126.1 (+, 2C), 122.0, 119.0, 114.2 (+, 2C), 95.9 (+), 55.5 (+), 42.2 (-), 39.0 (-), 35.2, 13.9 (+), 12.8 (+); FTIR (KBr, cm^{-1}): 2972, 2934, 1752, 1625, 1505, 1442, 1250, 1177, 1030, 835, 700; HRMS (TOF ES): Found 322.1799, calculated for $\text{C}_{21}\text{H}_{24}\text{NO}_2$ ($\text{M}+\text{H}$) 322.1807 (2.5 ppm).



N,N-diethyl-2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxamide (92e)

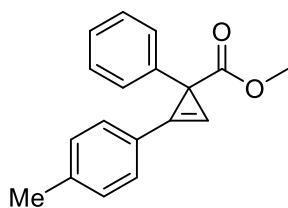
Compound was obtained via [typical amide procedure] using 2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylic acid (**96e**) (250 mg, 1.0 mmol, 1.0 equiv.). The product was then purified by silica gel column chromatography using a 2:1 hexane:ethyl acetate mobile phase to provide the titled compound as a pale yellow solid in 96% yield (299 mg, 0.966 mmol). mp: 86.6 – 89.1 °C; *R_f*: 0.29; ¹H NMR (500 MHz, CDCl₃) δ 7.82 – 7.70 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 7.22 – 7.17 (m, 1H), 7.05 (s, 1H), 7.05 – 6.99 (m, 2H), 3.56 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.49 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.36 – 3.22 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 173.2, 163.6 (d, *J* = 250.7 Hz), 142.4, 132.5 (+, d, *J* = 8.3 Hz, 2C), 128.6 (+, 2C), 126.4 (+), 126.1 (+, 2C), 122.7 (d, *J* = 2.9 Hz), 122.0, 115.9 (+, d, *J* = 21.9 Hz, 2C), 97.7 (+, d, *J* = 2.7 Hz), 42.2 (-), 39.0 (-), 35.5, 13.8 (+), 12.7 (+); ¹⁹F; FTIR (KBr, cm⁻¹): 2973, 2934, 1624, 1500, 1428, 1222, 839, 700; HRMS (TOF ES): Found 332.1426, calculated for C₂₀H₂₀FNONa (M+Na) 332.1427 (0.3 ppm).



N,N-diethyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxamide (92f)

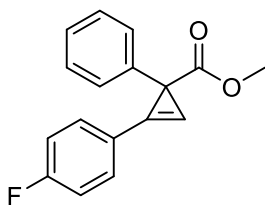
Compound was obtained via [typical amide procedure] using 1-phenyl-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxylic acid (**96f**) (230 mg, 0.760 mmol, 1.0 equiv.). The product was then purified by silica gel column chromatography using a 40:1 dichloromethane:ethyl acetate mobile phase to provide the titled compound as a colorless solid in 53% yield (146.1 mg, 0.406 mmol). mp: 80.0 – 82.4 °C; *R_f*: 0.29; ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.15 (m, 6H), 3.62 – 3.43 (m, 2H), 3.38 – 3.24 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ¹³C NMR

(126 MHz, CDCl₃) δ 172.8, 142.0, 131.3 (q, J = 32.3 Hz), 130.6 (+, 2C), 129.9, 128.7 (+, 2C), 126.7 (+), 126.1 (+, 2C), 125.7 (q, J = 3.8 Hz, +, 2C), 124.0 (q, J = 272.4 Hz), 122.3, 101.3 (+), 42.2 (-), 39.1 (-), 35.8, 13.9 (+), 12.7 (+); ¹⁹F NMR (376 MHz, CDCl₃) δ -62.85 (s, 3F); FTIR (KBr, cm⁻¹): 3082, 2976, 2936, 1626, 1430, 1323, 1277, 1166, 1124, 1064, 846, 712, 699; HRMS (TOF ES): Found 382.1385, calculated for C₂₁H₂₀F₃NONa (M+Na) 382.1395 (2.6 ppm).



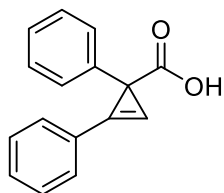
methyl 1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxylate (95d)

p-tolylacetylene (1.0 g, 8.61 mmol, 1.5 equiv.) and rhodium(II) acetate dimer (25.0 mg, 0.115 mmol, 0.02 equiv.) in 7 mL dichloromethane were placed in 25 mL 2-neck flask under inert nitrogen atmosphere at room temperature. methyl 2-diazo-2-phenylacetate (**17a**) (1.0 g, 5.74 mmol, 1.0 equiv.) diluted in 5 mL DCM was then added via syringe pump over 18 hours and then stirred for an additional 3 hours. The reaction mixture was then evaporated and purified by silica gel column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow solid in 50% yield (761 mg, 2.88 mmol). mp: 73.1 – 75.9 °C; R_f : 0.26; ¹H NMR (500 MHz, CDCl₃) δ 7.57 – 7.53 (m, 2H), 7.44 – 7.40 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 7.16 (s, 1H), 3.74 (s, 3H), 2.40 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 175.3, 141.2, 140.5, 130.0 (+, 2C), 129.7 (+, 2C), 128.3 (+, 2C), 128.1 (+, 2C), 126.5 (+), 122.7, 117.1, 99.2 (+), 52.2 (+), 33.5, 21.7 (+); FTIR (KBr, cm⁻¹): 3025, 2948, 1719, 1504, 1433, 1210, 1020, 820, 699; HRMS (TOF ES): Found 287.1053, calculated for C₁₈H₁₆O₂Na (M+Na) 287.1048 (1.7 ppm).



methyl 2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylate (95e)

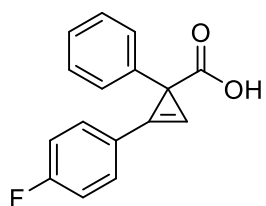
1-ethynyl-4-fluorobenzene (1.0 g, 8.32 mmol, 1.5 equiv.) and rhodium(II) acetate dimer (25.0 mg, 0.111 mmol, 0.02 equiv.) in 6 mL Dichloromethane were placed in 25 mL 2-neck flask under inert nitrogen atmosphere at room temperature. methyl 2-diazo-2-phenylacetate (**17a**) (977 mg, 5.55 mmol, 1.0 equiv.) diluted in 5 mL DCM was then added via syringe pump over 18 hours and then stirred for an additional 3 hours. The reaction mixture was then evaporated and purified by silica gel column chromatography using 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as an amorphous solid in 81% yield (1.21 g, 4.51 mmol). *R_f*: 0.26; ¹H NMR (500 MHz, CDCl₃) δ 7.66 – 7.60 (m, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 7.20 (s, 1H), 7.17 – 7.10 (m, 2H), 3.73 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 174.9, 163.6 (d, *J* = 251.0 Hz), 140.7, 131.9 (+, d, *J* = 9.0 Hz, 2C), 128.2 (+, 2C), 128.1 (+, 2C), 126.6 (+), 121.8 (d, *J* = 3.5 Hz), 116.5, 116.2 (+, d, *J* = 21.9 Hz, 2C), 99.8 (+, d, *J* = 2.7 Hz), 52.3 (+), 33.7; ¹⁹F NMR (376 MHz, CDCl₃) δ -109.1 (s, 1F); FTIR (KBr, cm⁻¹): 2951, 1723, 1599, 1503, 1434, 1223, 1014, 840, 699; HRMS (TOF ES): Found 291.0803, calculated for C₁₇H₁₃FO₂Na (M+Na) 291.0797 (2.1 ppm).



1,2-diphenylcycloprop-2-ene-1-carboxylic acid (96a)

Compound was obtained via [typical hydrolysis procedure] using methyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (**95a**) (500 mg, 2.0 mmol, 1.0 equiv.). The titled compound was obtained as an amorphous glass in 87% yield (411 mg, 1.74 mmol). ¹H NMR (500 MHz, CDCl₃): δ 7.66 – 7.60 (m, 2H), 7.47 – 7.38 (m, 5H), 7.30 – 7.26 (m, 2H), 7.23 – 7.19 (m, 2H); ¹³C (126 MHz, CDCl₃): δ 180.8, 140.0, 130.2 (+), 130.0 (+, 2C), 128.9 (+, 2C), 128.4 (+, 2C), 128.1 (+, 2C), 126.7 (+), 125.0, 116.9, 99.7 (+), 33.2; FTIR (KBr, cm⁻¹): 3138, 3059,

3003, 2887, 2839, 1639, 1682, 1487, 1446, 1414, 1256, 1224, 976, 953, 916, 764, 698; HRMS (TOF ES): Found 259.0742, calculated for C₁₆H₁₂O₂Na (M+Na) 259.0735 (2.7 ppm).

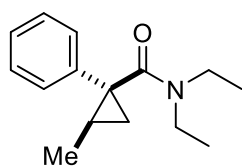


2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylic acid

(96e)

A solution of methyl 2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxylate **(95e)** (300 mg, 1.12 mmol, 1.0 equiv.) in a 1:1 mixture of methanol:tetrahydrofuran (20 mL) was stirred at 0 °C. A 1.5 M aqueous solution of sodium hydroxide (8 mL) was added dropwise and the mixture was stirred for 18 hours. Organic solvents were then removed under vacuum and the remaining aqueous solution was added to dichloromethane (20 mL). The mixture was acidified to pH 2 with 1N aqueous HCl. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic phases were washed with brine, dried with MgSO₄, filtered, and concentrated. The obtained product is typically pure enough to be used in further amide coupling as is, however, if necessary, further purification can be achieved by column chromatography on silica gel using a 1:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 90 % yield (257 mg, 1.01 mmol). mp: 138.9 – 140.2 °C; *R*_f: 0.26; ¹H NMR (500 MHz, CDCl₃) δ 7.64 – 7.59 (m, 2H), 7.41 – 7.37 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.18 (s, 1H), 7.15 – 7.09 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 179.8, 163.8 (d, *J* = 251.6 Hz), 139.9, 132.1 (+, d, *J* = 9.0 Hz, 2C), 128.4 (+, 2C), 128.3 (+, 2C), 127.0 (+), 121.5 (d, *J* = 2.9 Hz), 116.4 (+, d, *J* = 21.9 Hz, 2C), 116.3, 99.4 (+, d, *J* = 2.9 Hz), 33.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -108.8 (s, 1F); FTIR (KBr, cm⁻¹): 3138, 3025, 1686, 1599, 1502, 1408, 1227, 837, 698; HRMS (TOF ES): Found 277.0645, calculated for C₁₆H₁₁FO₂Na (M+Na) 277.0641 (1.4 ppm).

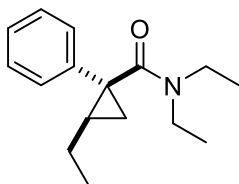
3.13.2 Carbomagnesiation Followed by Protic Quench



(1*S,2*R**)-N,N-diethyl-2-methyl-1-phenylcyclopropane-1-carboxamide (71a)**

[Typical Procedure A]: Methylmagnesium bromide (135 μ L, 3.0 M

(diethyl ether), 0.405 mmol, 1.35 equiv.) was added dropwise to a flame dried two neck flask containing copper iodide (3.0 mg, 15.0 μ mol, 5.0 mol%) and freshly dried and distilled dimethoxyethane (1.0 mL) under a nitrogen atmosphere at 0 °C. The mixture was stirred for five minutes at 0 °C. N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.) was then added slowly dropwise as a solution in dry dimethoxyethane (1.0 mL). After five minutes of stirring at 0 °C, saturated aqueous ammonium chloride (1 mL) was added dropwise and the reaction was stirred for another five minutes at 0 °C. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 96% yield (66.4 mg, 0.287 mmol). *R*_f: 0.45; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.11 (m, 5H), 3.69 – 3.46 (m, 2H), 3.18 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.07 (dq, *J* = 14.0, 7.0 Hz, 1H), 1.96 – 1.81 (m, 1H), 1.40 (dd, *J* = 6.3, 4.6 Hz, 1H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.85 (dd, *J* = 8.8, 4.6 Hz, 1H), 0.54 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.5, 141.9, 128.7 (+, 2C), 126.2 (+, 3C), 41.4 (-), 39.2 (-), 35.5, 23.6 (-), 18.3 (+), 14.7 (+), 12.7 (+), 12.5 (+); FTIR (KBr, cm⁻¹): 3059, 3001, 2969, 2933, 2872, 1643, 1600, 1494, 1444, 1417, 1381, 1363, 1348, 1317, 1298, 1278, 1236, 1220, 1139, 1103, 1091, 761, 736; HRMS (TOF ES): Found 254.1528, calculated for C₁₅H₂₁NONa (M+Na) 254.1521 (2.8 ppm).

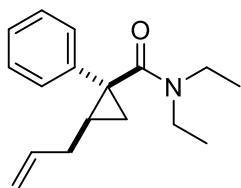


(1*S,2*R**)-N,N,2-triethyl-1-phenylcyclopropane-1-carboxamide**

(71g)

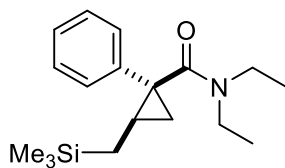
[Typical Procedure B]: Ethylmagnesium bromide (135 μ L, 3.0 M (diethyl

ether), 0.405 mmol, 1.35 equiv.) was added dropwise to a flame dried two neck flask containing copper iodide (3.0 mg, 15.0 μ mol, 5.0 mol%) and freshly dried and distilled dimethoxyethane (1.0 mL) under a nitrogen atmosphere at -45 $^{\circ}$ C. The mixture was stirred for five minutes at -45 $^{\circ}$ C. N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.) was then added slowly dropwise as a solution in dry dimethoxyethane (1.0 mL). The reaction was then stirred for 60 minutes at -45 $^{\circ}$ C. Water was then added very slowly dropwise. After ten minutes of stirring, saturated aqueous ammonium chloride (1 mL) was added and the reaction was allowed to warm to room temperature. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 83% yield (61.1 mg, 0.249 mmol). *R*_f: 0.42; dr: >99:1; 1 H NMR (500 MHz, CDCl₃) δ 7.36 – 7.13 (m, 5H), 3.67 – 3.47 (m, 2H), 3.17 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.05 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.76 – 1.68 (m, 1H), 1.40 (dd, *J* = 6.3, 4.6 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.99 – 0.93 (m, 1H), 0.84 (dd, *J* = 8.8, 4.5 Hz, 1H), 0.53 (t, *J* = 7.1 Hz, 3H); 13 C NMR (126 MHz, CDCl₃) δ 170.6, 142.0, 128.7 (+, 2C), 126.3 (+, 2C), 126.2 (+), 41.6 (-), 39.3 (-), 35.7, 26.1 (+), 23.1 (-), 22.2 (-), 13.8 (+), 12.7 (+), 12.5 (+); FTIR (KBr, cm⁻¹): 3059, 3024, 2966, 2931, 2872, 1643, 1600, 1494, 1444, 1417, 1381, 1361, 1346, 1315, 1298, 1276, 1220, 1139, 1099, 1068, 771, 754; HRMS (TOF ES): Found 268.1684, calculated for C₁₆H₂₃NONa (M+Na) 268.1677 (2.6 ppm).



(1*S,2*R**)-2-allyl-N,N-diethyl-1-phenylcyclopropane-1-carboxamide (71b)**

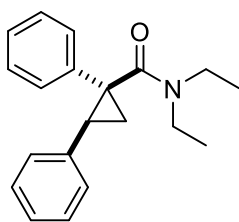
Compound was obtained via [typical procedure A] using allylmagnesium bromide (405 μ L, 1.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless oil in 94% yield (72.2 mg, 0.280 mmol). R_f : 0.39; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.24 (m, 2H), 7.24 – 7.13 (m, 3H), 5.93 (dddd, J = 17.1, 10.2, 6.9, 5.9 Hz, 1H), 5.13 (dd, J = 17.2, 1.7 Hz, 1H), 5.03 (dd, J = 10.3, 1.7 Hz, 1H), 3.69 – 3.49 (m, 2H), 3.18 (dq, J = 14.0, 7.1 Hz, 1H), 3.04 (dq, J = 14.1, 7.0 Hz, 1H), 2.46 – 2.32 (m, 1H), 1.96 – 1.84 (m, 1H), 1.84 – 1.72 (m, 1H), 1.48 (dd, J = 6.3, 4.7 Hz, 1H), 1.11 (t, J = 7.1 Hz, 3H), 0.92 (dd, J = 8.8, 4.7 Hz, 1H), 0.52 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.3, 141.7, 137.2 (+), 128.7 (+, 2C), 126.4 (+, 2C), 126.4 (+), 115.4 (-), 41.8 (-), 39.4 (-), 35.4, 34.0 (-), 23.5 (+), 22.1 (-), 12.6 (+), 12.6 (+); FTIR (KBr, cm^{-1}): 3076, 3063, 2976, 2933, 2874, 1643, 1633, 1494, 1442, 1427, 1381, 1363, 1346, 1317, 1296, 1278, 1238, 1220, 1139, 1101, 1078, 1031, 995, 912, 761; HRMS (TOF ES): Found 280.1683, calculated for $\text{C}_{17}\text{H}_{23}\text{NONa}$ ($\text{M}+\text{Na}$) 280.1677 (2.1 ppm).



(1*S,2*R**)-N,N-Diethyl-1-phenyl-2-((trimethylsilyl)methyl)cyclopropane-1-carboxamide (71c)**

Compound was obtained via [Typical Procedure A] using (trimethylsilyl)methylmagnesium chloride (1.86 mL, 1.3 M (tetrahydrofuran), 2.42 mmol, 1.30 equiv.), copper iodide (18.0 mg, 0.093 mmol, 0.05 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (400.0 mg, 1.86 mmol, 1.0 equiv.), and quenched with excess water. The product was purified by column chromatography using silica and a 2:1 hexane:diethyl ether

mobile phase. The titled compound was obtained as colorless oil in 84% yield (475 mg, 1.56 mmol). *R*_f: 0.34; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.26 (m, 1H), 7.25 (s, 1H), 7.21 – 7.14 (m, 3H), 3.65 – 3.48 (m, 2H), 3.24 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.08 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.82 (dddd, *J* = 12.3, 8.9, 6.3, 2.6 Hz, 1H), 1.38 (dd, *J* = 6.4, 4.6 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.93 (dd, *J* = 14.3, 2.6 Hz, 1H), 0.90 (dd, *J* = 8.8, 4.7 Hz, 1H), 0.56 (t, *J* = 7.1 Hz, 3H), 0.15 (dd, *J* = 14.3, 12.3 Hz, 1H), 0.08 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 172.1, 143.5, 130.0 (+, 2C), 127.6 (+, 2C), 127.5 (+), 42.8 (-), 40.6 (-), 36.8, 25.4 (-), 21.5 (+), 18.0 (-), 14.1 (+), 14.0 (+), 0.0 (+, 3C); FTIR (KBr, cm⁻¹): 2953, 2874, 1634, 1496, 1457, 1442, 1425, 1379, 1273, 1247, 861, 844, 785, 699; HRMS (TOF ES): Found 326.1926, calculated for C₁₈H₂₉NOSiNa (M+Na) 326.1916 (3.1 ppm).

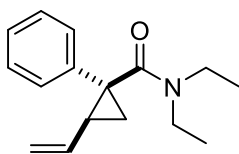


(1*S,2*S**)-N,N-diethyl-1,2-diphenylcyclopropane-1-carboxamide**

(71d)

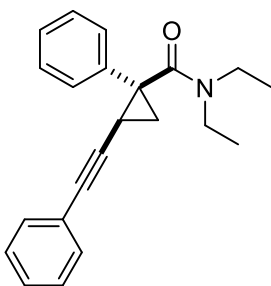
Compound was obtained via [typical procedure A] using phenylmagnesium bromide (135 μL, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 93% yield (82.2 mg, 0.280 mmol). *R*_f: 0.32; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.14 (m, 10H), 3.41 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.31 (dq, *J* = 14.2, 7.2 Hz, 1H), 3.10 (dd, *J* = 9.1, 6.9 Hz, 1H), 2.81 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.52 (dq, *J* = 14.1, 7.0 Hz, 1H), 2.33 (dd, *J* = 6.9, 5.4 Hz, 1H), 1.27 (dd, *J* = 9.1, 5.4 Hz, 1H), 0.66 (t, *J* = 7.1 Hz, 3H), 0.26 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.6, 141.3, 137.2, 128.8 (+, 2C), 128.2 (+, 2C), 127.4 (+, 2C), 126.6 (+), 126.5 (+), 126.1 (+, 2C), 41.0 (-), 40.4, 38.7 (-), 29.3 (+), 22.5 (-), 12.1 (+), 11.8 (+); FTIR (KBr, cm⁻¹): 3294, 3242, 3201, 3086, 3061, 3026, 3009, 2976, 2935, 2874, 1633, 1606, 1589, 1494, 1444, 1429, 1381, 1361,

1317, 1274, 1236, 1220, 1138, 771, 754, 732; HRMS (TOF ES): Found 316.1678, calculated for $C_{20}H_{23}NONa$ ($M+Na$) 316.1677 (0.3 ppm).



(1*S,2*S**)-N,N-diethyl-1-phenyl-2-vinylcyclopropane-1-carboxamide (71e)**

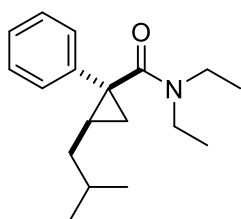
Compound was obtained via [typical procedure A] using vinylmagnesium bromide (405 μ L, 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.) and N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 97% yield (70.8 mg, 0.291 mmol). R_f : 0.39; dr: >99:1; 1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.17 (m, 5H), 5.46 – 5.35 (m, 1H), 5.28 (dd, J = 17.0, 1.7 Hz, 1H), 5.05 (dd, J = 10.1, 1.7 Hz, 1H), 3.57 – 3.49 (m, 1H), 3.49 – 3.40 (m, 1H), 3.17 (dq, J = 14.0, 7.0 Hz, 1H), 3.01 (dq, J = 14.2, 7.0 Hz, 1H), 2.60 – 2.51 (m, 1H), 1.80 (dd, J = 6.2, 4.9 Hz, 1H), 1.13 – 1.05 (m, 4H), 0.55 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 140.9, 136.7 (+), 128.8 (+, 2C), 126.6 (+), 126.0 (+, 2C), 115.8 (-), 41.3 (-), 39.3 (-), 37.2, 28.3 (+), 23.4 (-), 12.7 (+), 12.4 (+); FTIR (KBr, cm^{-1}): 3082, 3059, 3003, 2974, 2935, 2874, 1643, 1624, 1494, 1460, 1427, 1381, 1363, 1346, 1315, 1294, 1276, 1220, 1136, 1101, 1078, 1068, 1030, 989, 949, 902, 786, 759; HRMS (TOF ES): Found 244.1704, calculated for $C_{16}H_{22}NO$ ($M+H$) 244.1701 (1.2 ppm).



(1*S,2*S**)-N,N-diethyl-1-phenyl-2-(phenylethynyl)cyclopropane-1-carboxamide (71h)**

Methylmagnesium bromide (150 μ L, 3.0 M (diethyl ether), 0.450 mmol, 1.50 equiv.) was added slowly dropwise to a flame dried two neck flask

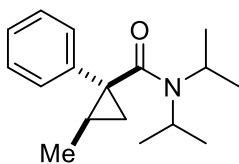
containing phenylacetylene (53.0 μ L, 0.480 mmol, 1.60 equiv.) and dry dimethoxyethane (1 mL) under a nitrogen atmosphere. The reaction was then stirred and heated at 55 $^{\circ}$ C for one hour. The solution was then cooled to room temperature and cannulated dropwise into another flame dried two neck flask containing copper iodide (3.0 mg, 15.0 μ mol, 5 mol%) and dry dimethoxyethane (1 mL) under a nitrogen atmosphere at 0 $^{\circ}$ C. After 5 minutes of stirring, N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.) as a solution in dry dimethoxyethane (1 mL) was added dropwise and the reaction was stirred for 60 minutes at 0 $^{\circ}$ C. Saturated aqueous ammonium chloride (1 mL) was then added dropwise. The resulting solution was diluted with water and extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous light yellow oil in 19% yield (18.8 mg, 0.06 mmol). R_f : 0.35; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.15 (m, 10H), 3.66 – 3.57 (m, 1H), 3.57 – 3.49 (m, 1H), 3.20 – 3.04 (m, 2H), 2.62 (dd, J = 9.0, 6.2 Hz, 1H), 2.03 (dd, J = 6.2, 4.6 Hz, 1H), 1.13 (dd, J = 9.0, 4.5 Hz, 1H), 0.99 (t, J = 7.1 Hz, 3H), 0.56 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.8, 139.6, 131.7 (+, 2C), 128.9 (+, 2C), 128.3 (+, 2C), 128.0 (+), 127.1 (+), 126.3 (+, 2C), 123.4, 88.0, 79.6, 41.7 (+), 39.6 (+), 38.3, 25.0 (+), 13.8 (-), 12.8 (-), 12.6 (-); FTIR (KBr, cm^{-1}): 3059, 2968, 2926, 2852, 1645, 1635, 1558, 1539, 1506, 1456, 1429, 1219, 1134, 1068, 1026, 945, 910, 842, 758; HRMS (TOF ES): Found 340.1689, calculated for $\text{C}_{22}\text{H}_{23}\text{NONa}$ ($\text{M}+\text{Na}$) 340.1677 (3.5 ppm).



(1*S,2*R**)-N,N-diethyl-2-isobutyl-1-phenylcyclopropane-1-carboxamide (71i)**

Compound was obtained via [typical procedure B] using isobutylmagnesium bromide (405 μ L, 1.0 M (tetrahydrofuran), 0.405

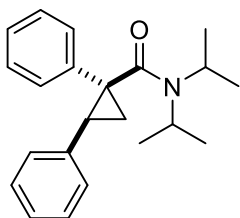
mmol, 1.35 equiv.) and N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 90% yield (74.2 mg, 0.271 mmol). *R*_f: 0.26; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.11 (m, 5H), 3.63 – 3.49 (m, 2H), 3.18 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.04 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.79 – 1.69 (m, 1H), 1.63 – 1.53 (m, 1H), 1.45 (dd, *J* = 6.4, 4.5 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.97 (d, *J* = 5.5 Hz, 3H), 0.96 (d, *J* = 6.1 Hz, 3H), 0.88 (dd, *J* = 8.8, 4.5 Hz, 1H), 0.84 – 0.77 (m, 1H), 0.52 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.6, 142.1, 128.7 (+, 2C), 126.4 (+, 2C), 126.3 (+), 41.6 (-), 39.3 (-), 38.5 (-), 34.7, 28.6 (+), 23.0 (-), 22.9 (+), 22.7 (+), 22.6 (+), 12.6 (+), 12.5 (+); FTIR (KBr, cm⁻¹): 3059, 2955, 2933, 2870, 1643, 1633, 1600, 1494, 1442, 1427, 1381, 1365, 1346, 1317, 1294, 1276, 1242, 1220, 1139, 1101, 1068, 1031, 759, 742; HRMS (TOF ES): Found 296.1978, calculated for C₁₈H₂₇NONa (M+Na) 296.1990 (4.1 ppm).



(1*S,2*R**)-N,N-diisopropyl-2-methyl-1-phenylcyclopropane-1-carboxamide (**73ba**)**

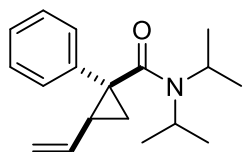
Compound was obtained via [typical procedure A] using Methylmagnesium bromide (135 μL, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and N,N-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ab**) (73.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 94% yield (73.2 mg, 0.282 mmol). *R*_f: 0.35; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.13 (m, 5H), 4.25 (hept, *J* = 6.6 Hz, 1H), 3.22 (hept, *J* = 6.8 Hz, 1H), 2.00 – 1.84 (m, 1H), 1.43 (d, *J* = 6.8 Hz, 3H), 1.41 (d, *J* = 7.0 Hz, 3H), 1.39 (dd, *J* = 6.25, 4.57 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H), 0.77 (dd, *J* = 8.9, 4.5 Hz, 1H), 0.36 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.1, 142.2, 128.6 (+, 2C),

126.6 (+, 2C), 126.2 (+), 48.9 (+), 45.9 (+), 37.2, 22.8 (-), 21.8 (+), 21.1 (+), 19.7 (+), 19.2 (+), 18.0 (+), 15.1 (+); FTIR (KBr, cm^{-1}): 3059, 2999, 2962, 2931, 2872, 1633, 1600, 1494, 1435, 1369, 1336, 1238, 1211, 1157, 1134, 1091, 1039, 734; HRMS (TOF ES): Found 282.1844, calculated for $\text{C}_{17}\text{H}_{25}\text{NONa}$ ($\text{M}+\text{Na}$) 282.1834 (3.5 ppm).



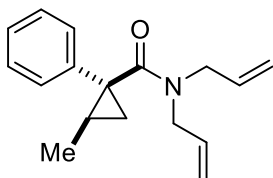
(1*S,2*S**)-N,N-diisopropyl-1,2-diphenylcyclopropane-1-carboxamide (73bd)**

Compound was obtained via [typical procedure A] using phenylmagnesium bromide (135 μL , 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and N,N-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ab**) (73.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 91% yield (87.8 mg, 0.273 mmol). mp: 132.8-135.5 $^{\circ}\text{C}$; R_f : 0.42; dr: 20:1; ^1H NMR (500 MHz, CDCl_3) δ 7.50 – 7.15 (m, 10H), 4.03 – 3.88 (m, 1H), 3.11 (dd, J = 9.3, 6.9 Hz, 1H), 3.01 – 2.89 (m, 1H), 2.24 (dd, J = 6.9, 5.3 Hz, 1H), 1.34 (d, J = 6.7 Hz, 3H), 1.23 (dd, J = 9.2, 5.3 Hz, 1H), 1.18 (d, J = 6.8 Hz, 3H), 0.21 (d, J = 6.6 Hz, 3H), 0.06 (d, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.4, 141.3, 138.2, 128.7 (+, 2C), 128.4 (+, 2C), 127.4 (+, 2C), 126.7 (+, 2C), 126.7 (+), 126.5 (+), 48.8 (+), 45.9 (+), 42.2, 28.5 (+), 23.2 (-), 20.3 (+), 20.2 (+), 19.5 (+), 19.1 (+); FTIR (KBr, cm^{-1}): 3059, 3028, 3007, 2960, 2931, 1620, 1496, 1469, 1444, 1369, 1342, 1209, 1157, 1134, 1122, 1078, 1057, 1037, 1022, 800, 773, 758, 734, 704; HRMS (TOF ES): Found 322.2172, calculated for $\text{C}_{22}\text{H}_{28}\text{NO}$ ($\text{M}+\text{H}$) 322.2171 (0.3 ppm).



(1*S,2*S**)-N,N-diisopropyl-1-phenyl-2-vinylcyclopropane-1-carboxamide (73be)**

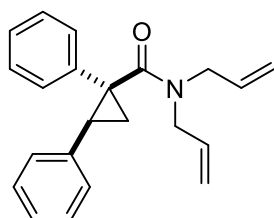
Compound was obtained via [typical procedure A] using vinylmagnesium bromide (405 μ L, 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.) and N,N-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ab**) (73.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 88% yield (71.8 mg, 0.265 mmol). *R*_f: 0.55; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.11 (m, 5H), 5.54 – 5.38 (m, 1H), 5.31 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.08 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.16 (hept, *J* = 6.6 Hz, 1H), 3.20 (hept, *J* = 6.8 Hz, 1H), 2.74 – 2.44 (m, 1H), 1.78 (dd, *J* = 6.1, 4.8 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.5 Hz, 3H), 1.02 – 0.98 (m, 1H), 0.35 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.3, 140.9, 137.3 (+), 128.7 (+, 2C), 126.6 (+), 126.4 (+, 2C), 115.5 (-), 49.0 (+), 45.9 (+), 38.8, 27.7 (+), 23.0 (-), 21.8 (+), 20.9 (+), 19.6 (+), 19.2 (+); FTIR (KBr, cm⁻¹): 3082, 3061, 3001, 2964, 2931, 2874, 1633, 1600, 1494, 1471, 1437, 1369, 1338, 1215, 1157, 1132, 1037, 989, 902, 761, 742, 700; HRMS (TOF ES): Found 272.2018, calculated for C₁₈H₂₆NO (M+H) 272.2014 (1.5 ppm).



(1*S,2*R**)-N,N-diallyl-2-methyl-1-phenylcyclopropane-1-carboxamide (73ca)**

Compound was obtained via [typical procedure A] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and N,N-diallyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ac**) (72.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 94% yield (71.6 mg,

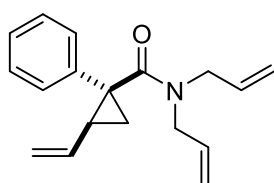
0.280 mmol). R_f : 0.29; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.14 (m, 5H), 5.83 – 5.65 (m, 1H), 5.22 – 5.05 (m, 2H), 4.97 – 4.88 (m, 3H), 4.35 – 4.24 (m, 1H), 4.21 – 4.11 (m, 1H), 3.72 – 3.53 (m, 2H), 1.94 – 1.86 (m, 1H), 1.43 (dd, J = 6.3, 4.6 Hz, 1H), 1.17 (d, J = 6.3 Hz, 3H), 0.91 (dd, J = 8.8, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.9, 141.6, 133.1 (+), 128.8 (+, 3C), 126.4 (+), 126.4 (+, 2C), 118.5 (-), 117.8 (-), 49.5 (-), 46.7 (-), 35.4, 23.4 (-), 18.7 (+), 15.0 (+); FTIR (KBr, cm^{-1}): 3078, 3005, 2980, 2958, 2928, 1643, 1633, 1600, 1496, 1454, 1435, 1410, 1332, 1300, 1280, 1263, 1209, 1193, 1138, 1112, 1095, 993, 923, 759, 731; HRMS (TOF ES): Found 278.1536, calculated for $\text{C}_{17}\text{H}_{21}\text{NONa}$ ($\text{M}+\text{Na}$) 278.1521 (5.4 ppm).



(1*S,2*S**)-N,N-diallyl-1,2-diphenylcyclopropane-1-carboxamide**
(73cd)

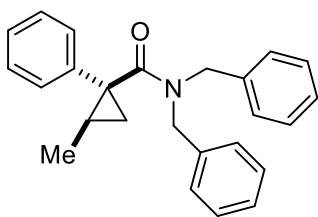
Compound was obtained via [typical procedure A] using phenylmagnesium bromide (135 μL , 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and N,N-diallyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ac**) (72.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 95% yield (90.6 mg, 0.285 mmol). mp: 111.5–113.9 $^{\circ}\text{C}$; R_f : 0.32; dr: 9:1; ^1H NMR (500 MHz, CDCl_3) δ 7.56 – 7.15 (m, 10H), 5.20 – 5.09 (m, 1H), 4.85 (d, J = 10.2 Hz, 1H), 4.78 (d, J = 10.1 Hz, 1H), 4.74 (d, J = 17.1 Hz, 1H), 4.64 (d, J = 17.2 Hz, 1H), 4.50 – 4.36 (m, 1H), 4.12 – 4.02 (m, 1H), 3.99 – 3.87 (m, 1H), 3.37 – 3.29 (m, 1H), 3.14 (dd, J = 9.1, 6.9 Hz, 1H), 3.12 – 3.06 (m, 1H), 2.38 (dd, J = 6.9, 5.5 Hz, 1H), 1.30 (dd, J = 9.1, 5.5 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.0, 141.0, 136.9, 132.8 (+), 132.6 (+), 128.9 (+, 2C), 128.4 (+, 2C), 127.6 (+, 2C), 126.9 (+), 126.7 (+), 126.4 (+, 2C), 118.5 (-), 117.3 (-), 49.4 (-), 46.2 (-), 40.4, 29.2 (+), 22.2 (-); FTIR (KBr, cm^{-1}): 3084, 3063, 3028, 3010, 2910, 1643, 1622, 1600, 1494, 1454, 1442, 1435, 1411, 1300, 1284, 1269, 1215, 1180, 1076, 1031, 991,

922, 902, 765, 734; HRMS (TOF ES): Found 340.1675, calculated for $C_{22}H_{23}NONa$ ($M+Na$) 340.1677 (0.6 ppm).



(1*S,2*S**)-N,N-diallyl-1-phenyl-2-vinylcyclopropane-1-carboxamide (73ce)**

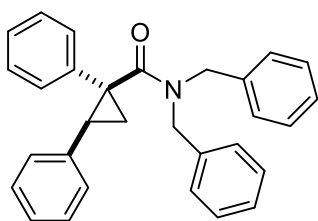
Compound was obtained via [typical procedure A] using vinylmagnesium bromide (405 μ L, 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.) and N,N-diallyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ac**) (72.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous light yellow oil in 80% yield (63.8 mg, 0.239 mmol). R_f : 0.45; dr: >99:1; 1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.10 (m, 5H), 5.87 – 5.60 (m, 1H), 5.57 – 5.37 (m, 1H), 5.37 – 5.27 (m, 1H), 5.22 – 5.02 (m, 3H), 5.00 – 4.82 (m, 3H), 4.30 – 4.15 (m, 1H), 4.12 – 3.93 (m, 1H), 3.77 – 3.45 (m, 2H), 2.70 – 2.41 (m, 1H), 1.83 (dd, J = 6.2, 5.0 Hz, 1H), 1.14 (dd, J = 8.7, 5.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 140.5, 136.6 (+), 133.2 (+), 132.9 (+), 128.9 (+, 2C), 126.8 (+), 126.2 (+, 2C), 118.6 (-), 117.7 (-), 116.2 (-), 49.6 (-), 46.6 (-), 37.2, 28.4 (+), 23.2 (-); FTIR (KBr, cm^{-1}): 3080, 3063, 3007, 2982, 1643, 1633, 1600, 1496, 1435, 1411, 1332, 1296, 1261, 1205, 1136, 1111, 1031, 993, 923, 758, 731, 700; HRMS (TOF ES): Found 290.1519, calculated for $C_{18}H_{21}NONa$ ($M+Na$) 290.1521 (0.7 ppm).



(1*S,2*R**)-N,N-dibenzyl-2-methyl-1-phenylcyclopropane-1-carboxamide (73da)**

Compound was obtained via [typical procedure A] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and N,N-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ad**) (102 mg,

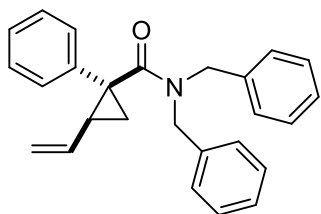
0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 95% yield (101 mg, 0.285 mmol). mp: 113.7-115.1 °C; R_f : 0.26; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.10 (m, 13H), 6.70 – 6.54 (m, 2H), 4.91 (d, J = 14.4 Hz, 1H), 4.80 (d, J = 15.6 Hz, 1H), 4.24 (d, J = 15.6 Hz, 1H), 4.01 (d, J = 14.4 Hz, 1H), 1.96 – 1.81 (m, 1H), 1.44 (dd, J = 6.3, 4.6 Hz, 1H), 1.25 (d, J = 6.3 Hz, 3H), 1.02 (dd, J = 8.8, 4.6 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.9, 141.4, 137.4, 136.0, 129.0 (+, 2C), 128.8 (+, 2C), 128.5 (+, 2C), 128.4 (+, 2C), 127.6 (+, 2C), 127.4 (+), 127.4 (+), 127.2 (+, 2C), 126.6 (+), 49.9 (-), 47.1 (-), 35.6, 22.5 (-), 19.3 (+), 15.6 (+); FTIR (KBr, cm^{-1}): 3061, 3028, 3003, 2956, 2928, 2868, 2359, 2341, 1633, 1600, 1494, 1450, 1417, 1361, 1317, 1296, 1193, 1078, 1028, 989, 752, 732; HRMS (TOF ES): Found 378.1842, calculated for $\text{C}_{25}\text{H}_{25}\text{NONa}$ ($\text{M}+\text{Na}$) 378.1834 (2.1 ppm).



(1*S,2*S**)-N,N-dibenzyl-1,2-diphenylcyclopropane-1-carboxamide (73dd)**

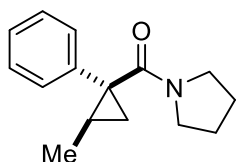
Compound was obtained via [typical procedure A] using phenylmagnesium bromide (135 μL , 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and N,N-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ad**) (102 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous light yellow oil in 93% yield (117 mg, 0.280 mmol). R_f : 0.30; dr: 13:1; ^1H NMR (500 MHz, CDCl_3) δ 7.50 – 7.41 (m, 2H), 7.36 – 6.93 (m, 14H), 6.69 – 6.56 (m, 2H), 6.19 – 6.05 (m, 2H), 4.58 (d, J = 14.7 Hz, 1H), 4.57 (d, J = 15.36 Hz, 1H), 3.88 (d, J = 14.8 Hz, 1H), 3.76 (d, J = 15.4 Hz, 1H), 3.20 (dd, J = 9.2, 7.0 Hz, 1H), 2.46 (dd, J = 7.0, 5.3 Hz, 1H), 1.34 (dd, J = 9.2, 5.3 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.2, 141.1, 137.1, 136.5, 135.4, 129.0 (+, 2C), 128.8 (+, 2C), 128.5 (+, 2C), 128.2 (+, 2C), 128.2

(+, 2C), 127.8 (+, 2C), 127.8 (+, 2C), 127.5 (+, 2C), 127.2 (+), 127.1 (+), 126.9 (+), 126.8 (+), 50.0 (-), 46.9 (-), 40.9, 29.0 (+), 21.3 (-); FTIR (KBr, cm^{-1}): 3086, 3061, 3028, 3009, 1643, 1604, 1591, 1583, 1494, 1454, 1417, 1361, 1313, 1294, 1267, 1209, 1182, 1078, 1030, 1012, 945, 779, 731; HRMS (TOF ES): Found 440.1988, calculated for $\text{C}_{30}\text{H}_{27}\text{NONa}$ ($\text{M}+\text{Na}$) 440.1990 (0.5 ppm).



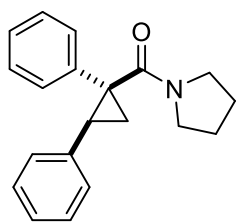
(1S*,2S*)-N,N-dibenzyl-1-phenyl-2-vinylcyclopropane-1-carboxamide (73de)

Compound was obtained via [typical procedure A] using vinylmagnesium bromide (405 μL , 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.) and N,N-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ad**) (102 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 84% yield (92.4 mg, 0.251 mmol). R_f : 0.52; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.46 – 7.02 (m, 13H), 6.71 – 6.44 (m, 2H), 5.64 – 5.47 (m, 1H), 5.30 (d, J = 17.0 Hz, 1H), 5.03 (d, J = 10.2 Hz, 1H), 4.87 (d, J = 14.5 Hz, 1H), 4.72 (d, J = 15.6 Hz, 1H), 4.15 (d, J = 15.6 Hz, 1H), 3.96 (d, J = 14.5 Hz, 1H), 2.64 – 2.42 (m, 1H), 1.85 (dd, J = 6.2, 4.9 Hz, 1H), 1.22 (dd, J = 8.7, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.1, 140.3, 137.2, 136.7 (+), 135.8, 129.0 (+, 2C), 129.0 (+, 2C), 128.4 (+, 2C), 128.4 (+, 2C), 127.9 (+, 2C), 127.4 (+), 127.4 (+), 127.1 (+, 2C), 127.0 (+), 116.3 (-), 50.0 (-), 47.1 (-), 37.4, 28.5 (+), 22.2 (-); FTIR (KBr, cm^{-1}): 3084, 3061, 3028, 3005, 2822, 1643, 1633, 1600, 1494, 1448, 1417, 1361, 1315, 1267, 1190, 1078, 1030, 1010, 976, 947, 906, 750, 736, 700; HRMS (TOF ES): Found 368.2026, calculated for $\text{C}_{26}\text{H}_{26}\text{NO}$ ($\text{M}+\text{H}$) 368.2014 (3.3 ppm).



((1*S,2*R**)-2-methyl-1-phenylcyclopropyl)(pyrrolidin-1-yl)methanone (73ia)**

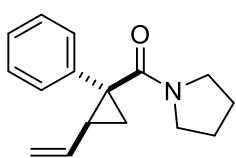
Compound was obtained via [typical procedure A] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (**53ai**) (64.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 91% yield (62.8 mg, 0.274 mmol). R_f : 0.16; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.14 (m, 5H), 3.57 – 3.48 (m, 2H), 3.41 – 3.32 (m, 1H), 2.91 – 2.79 (m, 1H), 1.91 – 1.79 (m, 2H), 1.79 – 1.64 (m, 3H), 1.44 (dd, J = 6.3, 4.6 Hz, 1H), 1.14 (d, J = 6.2 Hz, 3H), 0.89 (dd, J = 8.7, 4.6 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.6, 141.3, 128.7 (+, 2C), 126.2 (+, 2C), 126.2 (+), 47.1 (-), 46.3 (-), 36.6, 26.4 (-), 24.2 (-), 23.4 (-), 18.7 (+), 14.8 (+); FTIR (KBr, cm^{-1}): 3057, 2999, 2996, 2953, 2929, 2874, 1633, 1600, 1579, 1494, 1717, 1367, 1342, 1192, 1168, 1095, 1033, 912, 756, 734, 725, 700; HRMS (TOF ES): Found 252.1376, calculated for $\text{C}_{15}\text{H}_{19}\text{NONa}$ ($\text{M}+\text{Na}$) 252.1364 (4.8 ppm).



((1*S,2*S**)-1,2-diphenylcyclopropyl)(pyrrolidin-1-yl)methanone (73id)**

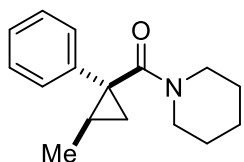
Compound was obtained via [typical procedure A] using phenylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (**53ai**) (64.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 87% yield (76.2 mg, 0.262 mmol). mp: 111.1–112.7 $^{\circ}\text{C}$; R_f : 0.16; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.16 (m, 10H), 3.38 – 3.24 (m, 1H), 3.10 – 2.93 (m, 3H), 2.71 – 2.57 (m, 1H), 2.33

(dd, $J = 6.9, 5.5$ Hz, 1H), 1.57 – 1.31 (m, 3H), 1.35 (dd, $J = 9.1, 5.6$ Hz, 1H), 0.96 – 0.75 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.7, 140.4, 137.5, 128.8 (+, 2C), 128.2 (+, 2C), 127.0 (+, 2C), 126.6 (+), 126.5 (+), 126.2 (+, 2C), 46.5 (-), 45.9 (-), 41.6, 29.9 (+), 25.6 (-), 23.8 (-), 22.7 (-); FTIR (KBr, cm^{-1}): 3057, 3028, 2970, 2874, 1626, 1579, 1496, 1448, 1427, 1340, 1190, 1168, 1122, 1078, 1031, 914, 873, 775, 763, 732; HRMS (TOF ES): Found 314.1523, calculated for $\text{C}_{20}\text{H}_{21}\text{NONa}$ ($\text{M}+\text{Na}$) 314.1521 (0.6 ppm).



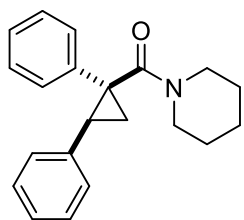
((1*S,2*S**)-1-phenyl-2-vinylcyclopropyl)(pyrrolidin-1-yl)methanone
(73ie)**

Compound was obtained via [typical procedure A] using phenylmagnesium bromide (135 μL , 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone **(53ai)** (64.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 82% yield (59.2 mg, 0.245 mmol). R_f : 0.16; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 5.51 – 5.35 (m, 1H), 5.30 (dd, $J = 17.0, 1.8$ Hz, 1H), 5.06 (dd, $J = 10.0, 1.8$ Hz, 1H), 3.61 – 3.43 (m, 2H), 3.45 – 3.31 (m, 1H), 2.90 – 2.71 (m, 1H), 2.55 – 2.39 (m, 1H), 1.86 – 1.77 (m, 1H), 1.83 (dd, $J = 6.2, 5.0$ Hz, 1H), 1.77 – 1.59 (m, 3H), 1.12 (dd, $J = 8.7, 4.9$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.9, 140.1, 136.9 (+), 128.8 (+, 2C), 126.5 (+), 126.1 (+, 2C), 115.9 (-), 46.7 (-), 46.4 (-), 38.4, 28.6 (+), 26.3 (-), 24.2 (-), 23.3 (-); FTIR (KBr, cm^{-1}): 3080, 3057, 3022, 3001, 2970, 2874, 1633, 1600, 1579, 1494, 1423, 1340, 1190, 1168, 1114, 1031, 993, 941, 910, 758, 727, 700; HRMS (TOF ES): Found 264.1377, calculated for $\text{C}_{16}\text{H}_{19}\text{NONa}$ ($\text{M}+\text{Na}$) 264.1364 (4.9 ppm).



((1*S,2*R**)-2-methyl-1-phenylcyclopropyl)(piperidin-1-yl)methanone (73ja)**

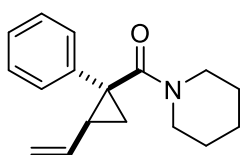
Compound was obtained via [typical procedure A] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(piperidin-1-yl)methanone (**53aj**) (68.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 90% yield (65.6 mg, 0.270 mmol). R_f : 0.16; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.11 (m, 5H), 3.82 – 3.71 (m, 1H), 3.49 – 3.35 (m, 2H), 3.31 – 3.20 (m, 1H), 1.92 – 1.81 (m, 1H), 1.59 – 1.44 (m, 4H), 1.38 (dd, J = 6.3, 4.7 Hz, 1H), 1.31 – 1.20 (m, 1H), 1.17 (d, J = 6.3 Hz, 3H), 1.09 – 0.96 (m, 1H), 0.91 (dd, J = 8.8, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.6, 141.9, 128.7 (+, 2C), 126.1 (+), 125.7 (+, 2C), 46.7 (-), 43.2 (-), 35.3, 25.8 (-), 25.7 (-), 24.6 (-), 24.0 (-), 19.4 (+), 15.3 (+); FTIR (KBr, cm^{-1}): 3059, 3001, 2935, 2854, 1633, 1600, 1496, 1465, 1433, 1294, 1271, 1259, 1211, 1138, 1128, 1022, 1003, 852, 754, 732, 700; HRMS (TOF ES): Found 266.1520, calculated for $\text{C}_{16}\text{H}_{21}\text{NONa}$ ($\text{M}+\text{Na}$) 266.1521 (0.4 ppm).



((1*S,2*S**)-1,2-diphenylcyclopropyl)(piperidin-1-yl)methanone (73jd)**

Compound was obtained via [typical procedure A] using phenylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(piperidin-1-yl)methanone (**53aj**) (68.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 89% yield (81.8 mg, 0.268 mmol). mp: 120.6-121.9 $^{\circ}\text{C}$; R_f : 0.29; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ

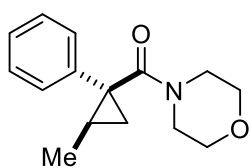
7.41 – 7.16 (m, 10H), 3.54 – 3.43 (m, 1H), 3.35 – 3.20 (m, 1H), 3.01 (dd, $J = 9.2, 7.0$ Hz, 1H), 2.98 – 2.91 (m, 1H), 2.88 – 2.81 (m, 1H), 2.26 (dd, $J = 7.0, 5.6$ Hz, 1H), 1.39 (dd, $J = 9.2, 5.6$ Hz, 1H), 1.38 – 1.30 (m, 1H), 1.27 – 1.18 (m, 2H), 1.16 – 1.05 (m, 1H), 0.90 – 0.80 (m, 1H), 0.33 – 0.20 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.7, 141.1, 137.8, 128.7 (+, 2C), 128.2 (+, 2C), 127.0 (+, 2C), 126.5 (+), 126.4 (+), 125.4 (+, 2C), 46.4 (-), 42.8 (-), 40.0, 30.9 (+), 25.0 (-), 25.0 (-), 24.1 (-), 23.6 (-); FTIR (KBr, cm^{-1}): 3057, 3028, 3005, 2935, 2854, 1631, 1496, 1437, 1292, 1271, 1247, 1217, 1136, 1124, 1078, 1031, 1012, 974, 852, 773, 761, 731; HRMS (TOF ES): Found 328.1682, calculated for $\text{C}_{21}\text{H}_{23}\text{NONa}$ ($\text{M}+\text{Na}$) 328.1677 (1.5 ppm).



((1*S,2*S**)-1-phenyl-2-vinylcyclopropyl)(piperidin-1-yl)methanone**
(73je)

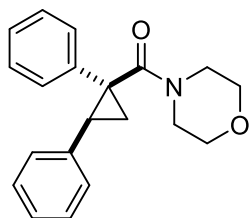
Compound was obtained via [typical procedure A] using vinylmagnesium bromide (405 μL , 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.) and (1-phenylcycloprop-2-en-1-yl)(piperidin-1-yl)methanone **(53aj)** (68.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 86% yield (66.0 mg, 0.258 mmol). R_f : 0.29; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 5.49 – 5.39 (m, 1H), 5.29 (dd, $J = 17.0, 1.6$ Hz, 1H), 5.07 (dd, $J = 10.2, 1.7$ Hz, 1H), 3.75 – 3.66 (m, 1H), 3.52 – 3.43 (m, 1H), 3.34 – 3.25 (m, 1H), 3.25 – 3.18 (m, 1H), 2.59 – 2.48 (m, 1H), 1.78 (dd, $J = 6.2, 5.0$ Hz, 1H), 1.55 – 1.44 (m, 4H), 1.32 – 1.23 (m, 1H), 1.15 (dd, $J = 8.7, 5.0$ Hz, 1H), 1.06 – 0.94 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.9, 140.9, 137.1 (+), 128.8 (+, 2C), 126.5 (+), 125.5 (+, 2C), 115.8 (-), 46.7 (-), 43.3 (-), 37.1, 29.4 (+), 25.8 (-), 25.7 (-), 24.5 (-), 23.8 (-); FTIR (KBr, cm^{-1}): 3080, 3059, 3003, 2935, 2854, 1643, 1626, 1496, 1435, 1369, 1352, 1271, 1257, 1207, 1136, 1126, 1103,

1031, 1010, 983, 952, 902, 852, 758, 742; HRMS (TOF ES): Found 278.1529, calculated for $C_{17}H_{21}NONa$ ($M+Na$) 278.1521 (2.9 ppm).



((1*S,2*R**)-2-methyl-1-phenylcyclopropyl)(morpholino)methanone (73ka)**

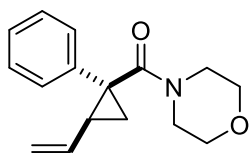
Compound was obtained via [typical procedure A] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and morpholino(1-phenylcycloprop-2-en-1-yl)methanone (**53ak**) (69.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 92% yield (67.6 mg, 0.276 mmol). R_f : 0.19; dr: >99:1; 1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.11 (m, 5H), 3.74 – 3.66 (m, 2H), 3.66 – 3.59 (m, 2H), 3.45 – 3.31 (m, 3H), 3.27 – 3.19 (m, 1H), 1.95 – 1.81 (m, 1H), 1.40 (dd, J = 6.4, 4.7 Hz, 1H), 1.19 (d, J = 6.2 Hz, 3H), 0.95 (dd, J = 8.8, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 141.4, 128.9 (+, 2C), 126.4 (+), 125.5 (+, 2C), 66.9 (-), 66.6 (-), 46.3 (-), 42.7 (-), 35.0, 23.9 (-), 19.3 (+), 15.3 (+); FTIR (KBr, cm^{-1}): 3062, 2999, 2960, 2920, 2899, 2854, 1639, 1496, 1456, 1427, 1390, 1359, 1301, 1273, 1209, 1114, 1095, 1068, 1030, 1008, 945, 912, 848, 756, 732, 700; HRMS (TOF ES): Found 268.1318, calculated for $C_{15}H_{19}NO_2Na$ ($M+Na$) 268.1313 (1.9 ppm).



((1*S,2*S**)-1,2-diphenylcyclopropyl)(morpholino)methanone (73kd)**

Compound was obtained via [typical procedure A] using phenylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and morpholino(1-phenylcycloprop-2-en-1-yl)methanone (**53ak**) (69.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1

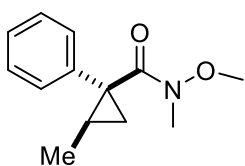
hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 81% yield (74.8 mg, 0.243 mmol). mp: 138.0-139.9 °C; *R*_f: 0.26; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.12 (m, 10H), 3.83 – 3.65 (m, 1H), 3.59 – 3.43 (m, 1H), 3.21 – 3.14 (m, 1H), 3.12 – 3.05 (m, 1H), 3.05 – 2.97 (m, 3H), 2.95 – 2.87 (m, 1H), 2.29 (dd, *J* = 7.0, 5.7 Hz, 1H), 2.15 – 2.08 (m, 1H), 1.42 (dd, *J* = 9.2, 5.7 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 168.0, 140.6, 137.5, 129.0 (+, 2C), 128.6 (+, 2C), 127.1 (+, 2C), 127.0 (+), 126.8 (+), 125.4 (+, 2C), 66.3 (-), 66.0 (-), 46.0 (-), 42.3 (-), 39.8, 31.0 (+), 23.3 (-); FTIR (KBr, cm⁻¹): 3057, 3028, 3003, 2962, 2922, 2897, 2854, 1639, 1599, 1496, 1458, 1431, 1359, 1301, 1274, 1215, 1190, 1112, 1068, 1031, 977, 898, 850, 773, 731; HRMS (TOF ES): Found 308.1666, calculated for C₂₀H₂₂NO₂ (M+H) 308.1651 (4.9 ppm).



morpholino((1*S,2*S**)-1-phenyl-2-vinylcyclopropyl)methanone**
(73ke)

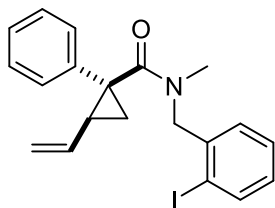
Compound was obtained via [typical procedure A] using vinylmagnesium bromide (405 μL, 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.) and morpholino(1-phenylcycloprop-2-en-1-yl)methanone (**53ak**) (69.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 83% yield (63.8 mg, 0.248 mmol). *R*_f: 0.16; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 – 7.14 (m, 2H), 5.51 – 5.38 (m, 1H), 5.30 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.12 (dd, *J* = 10.1, 1.6 Hz, 1H), 3.80 – 3.70 (m, 1H), 3.69 – 3.53 (m, 3H), 3.44 – 3.32 (m, 2H), 3.30 – 3.18 (m, 2H), 2.60 – 2.47 (m, 1H), 1.80 (dd, *J* = 6.2, 5.1 Hz, 1H), 1.18 (dd, *J* = 8.7, 5.1 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 169.2, 140.2, 136.8 (+), 129.0 (+, 2C), 126.8 (+), 125.3 (+, 2C), 116.3 (-), 66.8 (-), 66.7 (-), 46.3 (-), 42.6 (-), 36.6, 29.3 (+), 23.7 (-); FTIR (KBr, cm⁻¹): 3082, 3059, 3001, 2962, 2920, 2899, 2856, 1651, 1643, 1600, 1496, 1456, 1429, 1359, 1301, 1274, 1195, 1114, 1068, 1031, 985, 943, 908, 850,

758, 700; HRMS (TOF ES): Found 280.1309, calculated for C₁₆H₁₉NO₂Na (M+Na) 280.1313 (1.4 ppm).



(1*S,2*R**)-N-methoxy-N,2-dimethyl-1-phenylcyclopropane-1-carboxamide (73ua)**

Compound was obtained via [typical procedure A] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) and N-methoxy-N-methyl-1-phenylcycloprop-2-ene-1-carboxamide (**53au**) (61.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous light yellow oil in 90% yield (59.2 mg, 0.270 mmol). *R*_f: 0.39; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.14 (m, 5H), 3.12 (s, 3H), 3.05 (s (broad), 3H), 1.96 – 1.84 (m, 1H), 1.43 (dd, *J* = 6.4, 4.6 Hz, 1H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.85 (s (broad), 1H); ¹³C NMR (126 MHz, CDCl₃) δ 141.6, 128.5 (+, 2C), 127.5, 126.5 (+, 3C), 60.2, 35.7 (+), 33.3 (+), 22.0 (-), 18.4 (+), 14.5 (+); FTIR (KBr, cm⁻¹): 3059, 3001, 2962, 2931, 2874, 1660, 1651, 1600, 1496, 1442, 1410, 1365, 1172, 1122, 1101, 1074, 993, 908, 761; HRMS (TOF ES): Found 242.1165, calculated for C₁₃H₁₇NO₂Na (M+Na) 242.1157 (3.3 ppm).

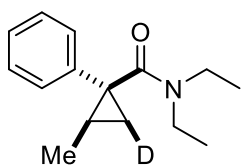


(1*S,2*S**)-N-(2-iodobenzyl)-N-methyl-1-phenyl-2-vinylcyclopropane-1-carboxamide (73ve)**

Compound was obtained via [typical procedure A] using vinylmagnesium bromide (1.15 mL, 1.0 M (tetrahydrofuran), 1.14 mmol, 1.30 equiv.) and N-(2-iodobenzyl)-N-methyl-1-phenylcycloprop-2-ene-1-carboxamide (**53av**) (340.0 mg, 0.873 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a

pale yellow oil in 89% yield (322 mg, 0.772 mmol). R_f : 0.26; dr: > 98:2; ^1H NMR (500 MHz, CDCl_3) : Mix of Rotomers: δ [7.80 (d, J = 7.9 Hz) & 7.66 (d, J = 7.8 Hz), $\Sigma 1\text{H}$], [7.39 – 7.30 (m) & 7.29 – 7.19 (m) & 7.15 – 7.11 (m) & 7.06 – 7.00 (m) & 6.97 – 6.90 (m) & 6.79 – 6.74 (m), $\Sigma 8\text{H}$], [5.63 – 5.48 (m), $\Sigma 1\text{H}$], [5.42 (dd, J = 17.0, 1.7 Hz) & 5.35 (dd, J = 17.0, 1.5 Hz), $\Sigma 1\text{H}$], [5.17 (dd, J = 10.0, 1.7 Hz) & 5.13 (dd, J = 10.2, 1.5 Hz), $\Sigma 1\text{H}$], [4.91 (d, J = 17.4 Hz) & 4.70 (d, J = 15.6 Hz), $\Sigma 1\text{H}$], [4.63 (d, J = 15.6 Hz) & 4.09 (d, J = 17.4 Hz), $\Sigma 1\text{H}$], [2.90 (s) & 2.73 (s), $\Sigma 3\text{H}$], [2.63 – 2.57 (m) & 2.57 – 2.50 (m), $\Sigma 1\text{H}$], [1.86 (dd, J = 6.3, 5.1 Hz) & 1.80 (dd, J = 6.2, 4.9 Hz), $\Sigma 1\text{H}$], [1.19 (dd, J = 8.7, 5.0 Hz) & 1.15 (dd, J = 8.7, 4.9 Hz), $\Sigma 1\text{H}$]; ^{13}C NMR (126 MHz, CDCl_3) : Mix of Rotomers: δ [171.6 & 170.9, $\Sigma 1\text{C}$], [140.1 & 139.6 (+) & 139.4 & 139.3 & 139.0 (+) & 137.9 & 136.7 (+) & 136.5 (+) & 129.0 (+) & 128.9 (+) & 128.6 (+) & 128.4 (+) & 128.3 (+) & 128.2 (+) & 128.0 (+) & 127.4 (+) & 126.8 (+) & 126.7 (+) & 126.6 (+) & 126.0 (+), $\Sigma 12\text{C}$], [116.6 (-) & 116.5 (-), $\Sigma 1\text{C}$], [99.1 & 97.5, $\Sigma 1\text{C}$], [58.7 (-) & 56.1 (-), $\Sigma 1\text{C}$], [37.6 & 37.2, $\Sigma 1\text{C}$], [35.4 (+) & 34.5 (+), $\Sigma 1\text{C}$], [28.9 (+) & 27.9 (+), $\Sigma 1\text{C}$], [23.2 (-) & 21.8 (-), $\Sigma 1\text{C}$]; FTIR (KBr, cm^{-1}): 3058, 3003, 2921, 1642, 1437, 1396, 1045, 907, 750; HRMS (TOF ES): Found 418.0680, calculated for $\text{C}_{20}\text{H}_{21}\text{INO}$ ($\text{M}+\text{H}$) 418.0668 (2.9 ppm).

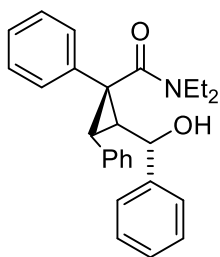
3.13.3 Carbomagnesiation Followed by Non-Protic Quench



(1*S,2*R**,3*S**)-N,N-diethyl-2-methyl-1-phenylcyclopropane-1-carboxamide-3-d (75)**

[Typical Procedure C]: Methylmagnesium bromide (135 μL , 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) was added dropwise to a flame dried two neck flask containing copper iodide (3.0 mg, 15.0 μmol , 5.0 mol%) and freshly dried and distilled dimethoxyethane (1.0 mL) under a nitrogen atmosphere at 0 $^\circ\text{C}$. The mixture was stirred for five minutes at 0 $^\circ\text{C}$. N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30

mmol, 1.0 equiv.) was then added slowly dropwise as a solution in dry dimethoxyethane (1.0 mL). After five minutes of stirring at 0 °C, methanol- d_4 (19.0 μ L, 16.5 mg, 0.45 mmol, 1.50 equiv.) was added dropwise and stirred for fifteen minutes at 0 °C. The reaction was then allowed to warm to room temperature over 15 minutes before saturated aqueous ammonium chloride (1 mL) was added. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 98% yield (68.4 mg, 0.294 mmol). R_f : 0.32; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 3.63 – 3.51 (m, 2H), 3.18 (dq, J = 14.0, 7.0 Hz, 1H), 3.07 (dq, J = 14.1, 7.0 Hz, 1H), 1.88 (dq, J = 8.8, 6.3 Hz, 1H), 1.13 (d, J = 6.3 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H), 0.84 (d, J = 8.7 Hz, 1H), 0.55 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.5, 142.0, 128.7 (+, 2C), 126.2 (+, 3C), 41.4 (-), 39.3 (-), 35.4, 23.3 (+, t, J = 24.5 Hz), 18.2 (+), 14.7 (+), 12.7 (+), 12.6 (+); FTIR (KBr, cm^{-1}): 3028, 3003, 2968, 2933, 2872, 1633, 1496, 1471, 1456, 1425, 1379, 1363, 1319, 1294, 1276, 1220, 1151, 1128, 1101, 1080, 1066, 868, 759, 732, 700; HRMS (TOF ES): Found 255.1586, calculated for $\text{C}_{15}\text{H}_{20}\text{DNONa}$ ($\text{M}+\text{Na}$) 255.1584 (0.8 ppm).

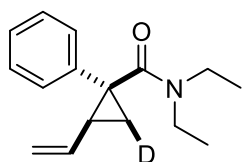


(1*R,2*R**,3*R**)-N,N-diethyl-2-((*R**)-hydroxy(phenyl)methyl)-1,3-diphenylcyclopropane-1-carboxamide (83da)**

[Typical Procedure D]: Phenylmagnesium bromide (130 μ L, 3.0 M (tetrahydrofuran), 0.39 mmol, 1.30 equiv.) was added dropwise to a flame

dried two neck flask containing copper iodide (3.0 mg, 15.0 μ mol, 5.0 mol%) and freshly dried and distilled dimethoxyethane (1.0 mL) under a nitrogen atmosphere at 0 °C. The mixture was stirred for five minutes at 0 °C. N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**)

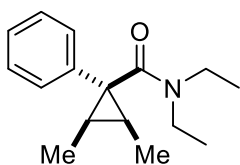
(65.0 mg, 0.30 mmol, 1.0 equiv.) was then added slowly dropwise as a solution in dry dimethoxyethane (1.0 mL). After fifteen minutes of stirring at 0 °C, freshly distilled benzaldehyde (48.0 mg, 46.0 μ L, 0.45 mmol, 1.5 equiv.) was added dropwise and stirred for thirty minutes at 0 °C. The reaction was then allowed to warm to room temperature over 15 minutes before saturated aqueous ammonium chloride (1 mL) was added. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography using silica and a 2:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as colorless solid in 80% yield (96.4 mg, 0.241 mmol). mp: 181.3 – 182.4 °C; R_f : 0.31; dr: 96:4; ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.33 (m, 2H), 7.30 – 7.25 (m, 5H), 7.24 – 7.15 (m, 3H), 7.09 – 7.03 (m, 3H), 6.94 – 6.89 (m, 2H), 5.14 (d, J = 10.4 Hz, 1H), 3.51 (dq, J = 14.1, 7.1 Hz, 1H), 3.29 (dq, J = 14.3, 7.2 Hz, 1H), 3.19 (dq, J = 14.1, 7.1 Hz, 1H), 3.13 (d, J = 10.1 Hz, 1H), 2.68 (dq, J = 14.2, 7.1 Hz, 1H), 1.64 (t, J = 10.3 Hz, 1H), 1.19 (s, 1H, broad), 1.11 (t, J = 7.1 Hz, 3H), 0.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.3, 143.4, 141.2, 136.1, 128.9 (+, 2C), 128.8 (+, 2C), 128.3 (+, 2C), 128.0 (+, 2C), 127.0 (+), 126.8 (+), 126.8 (+), 126.3 (+, 2C), 125.6 (+, 2C), 68.5 (+), 44.1 (+), 41.9 (-), 40.6, 39.3 (-), 32.4 (+), 11.9 (+), 11.9 (+); FTIR (KBr, cm^{-1}): 3355.3060, 3029, 2976, 2935, 1605, 1497, 1429, 1381, 1278, 1195, 1151, 741; HRMS (TOF ES): Found 422.2098, calculated for $\text{C}_{27}\text{H}_{29}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) 422.2096 (0.5 ppm).



(1*S,2*S**,3*S**)-N,N-diethyl-1-phenyl-2-vinylcyclopropane-1-carboxamide-3-d (76)**

Compound was obtained via [typical procedure C] using vinylmagnesium bromide (405 μ L, 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and methanol-

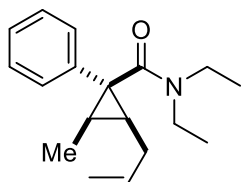
d₄ (19.0 μ L, 16.5 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 86% yield (63.2 mg, 0.259 mmol). *R*_f: 0.35; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 5.41 (ddd, *J* = 17.0, 10.1, 9.0 Hz, 1H), 5.28 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.05 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.61 – 3.38 (m, 2H), 3.17 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.01 (dq, *J* = 14.2, 7.1 Hz, 1H), 2.55 (dd, *J* = 8.9 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 8.9 Hz, 1H), 0.55 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.7, 140.9, 136.7 (+), 128.8 (+, 2C), 126.6 (+), 126.0 (+, 2C), 115.8 (-), 41.3 (-), 39.3 (-), 37.2, 28.2 (+), 23.1 (+, t, *J* = 25.2 Hz), 12.7 (+), 12.4 (+); FTIR (KBr, cm⁻¹): 3082, 3059, 2974, 2935, 2874, 1633, 1496, 1456, 1444, 1427, 1381, 1361, 1315, 1276, 1219, 1128, 991, 902, 756, 700; HRMS (TOF ES): Found 245.1770, calculated for C₁₆H₂₁DNO (M+H) 245.1764 (2.4 ppm).



(1*S,2*R**,3*S**)-N,N-diethyl-2,3-dimethyl-1-phenylcyclopropane-1-carboxamide (77a)**

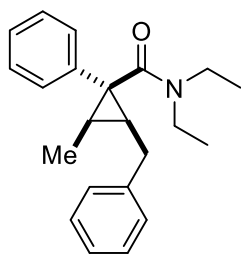
Compound was obtained via [typical procedure C] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and methyl iodide (28.0 μ L, 64.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 86% yield (63.2 mg, 0.258 mmol). *R*_f: 0.32; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 3.37 (q, *J* = 7.2 Hz, 2H), 3.32 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 2H), 1.21 (d, *J* = 6.4 Hz, 6H), 1.11 (d, *J* = 7.1 Hz, 3H), 0.59 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.5, 143.0, 128.6 (+, 2C), 126.0 (+), 125.7 (+, 2C), 41.4 (-), 38.4 (-), 35.9, 25.1 (+, 2C), 13.0 (+), 12.6 (+), 10.0 (+, 2C); FTIR (KBr, cm⁻¹): 3057, 3003, 2970, 2931,

2872, 1633, 1496, 1458, 1444, 1423, 1379, 1363, 1346, 1319, 1298, 1278, 1238, 1220, 1155, 1116, 1093, 1078, 756, 732; HRMS (TOF ES): Found 268.1669, calculated for C₁₆H₂₃NONa (M+Na) 268.1677 (3.0 ppm).



(1*R,2*S**,3*R**)-2-allyl-N,N-diethyl-3-methyl-1-phenylcyclopropane-1-carboxamide (77b)**

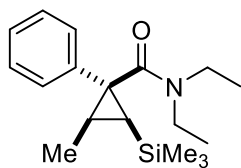
Compound was obtained via [typical procedure C] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and allyl bromide (39.0 μ L, 55.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 87% yield (70.6 mg, 0.260 mmol). *R*_f: 0.38; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.14 (m, 5H), 6.09 – 5.85 (m, 1H), 5.09 (dd, *J* = 17.2, 1.9 Hz, 1H), 4.99 (dd, *J* = 10.2, 2.0 Hz, 1H), 3.55 – 3.36 (m, 2H), 3.34 – 3.16 (m, 2H), 2.74 – 2.55 (m, 1H), 2.26 – 2.09 (m, 1H), 1.82 – 1.68 (m, 1H), 1.36 – 1.25 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.56 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 169.4, 142.7, 138.4 (+), 128.7 (+, 2C), 126.1 (+), 125.9 (+, 2C), 114.6 (-), 41.5 (-), 38.6 (-), 36.1, 31.2 (+), 29.8 (-), 22.9 (+), 12.9 (+), 12.6 (+), 9.9 (+); FTIR (KBr, cm⁻¹): 3061, 3003, 2972, 2933, 2874, 1633, 1600, 1496, 1458, 1423, 1379, 1363, 1346, 1319, 1298, 1278, 1240, 1220, 1155, 1120, 1101, 1078, 995, 908, 817; HRMS (TOF ES): Found 294.1840, calculated for C₁₈H₂₅NONa (M+Na) 294.1834 (2.0 ppm).



(1*R,2*S**,3*R**)-2-benzyl-N,N-diethyl-3-methyl-1-**

phenylcyclopropane-1-carboxamide (77c)

Compound was obtained via [typical procedure C] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and benzyl bromide (54.0 μ L, 77.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 82% yield (78.8 mg, 0.245 mmol). mp: 86.0-86.9 $^{\circ}$ C; R_f : 0.29; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.44 – 7.08 (m, 10H), 3.54 (dq, J = 14.8, 7.5 Hz, 1H), 3.47 (dq, J = 14.2, 7.1 Hz, 1H), 3.41 (dd, J = 15.6, 4.5 Hz, 1H), 3.32 – 3.17 (m, 2H), 2.76 (dd, J = 15.6, 9.9 Hz, 1H), 1.88 (dq, J = 9.5, 6.5 Hz, 1H), 1.52 – 1.43 (m, 1H), 1.27 (d, J = 6.5 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H), 0.57 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.5, 142.6, 142.3, 128.7 (+, 2C), 128.6 (+, 2C), 128.4 (+, 2C), 126.2 (+), 125.8 (+, 3C), 41.5 (-), 38.6 (-), 36.3, 33.6 (+), 31.3 (-), 22.6 (+), 12.9 (+), 12.7 (+), 10.2 (+); FTIR (KBr, cm^{-1}): 3082, 3059, 3024, 2970, 2933, 2874, 1633, 1600, 1494, 1454, 1423, 1379, 1363, 1346, 1319, 1298, 1278, 1240, 1220, 1153, 1112, 1103, 1078, 1030, 947, 864; HRMS (TOF ES): Found 344.1995, calculated for $\text{C}_{22}\text{H}_{27}\text{NONa}$ ($\text{M}+\text{Na}$) 344.1990 (1.5 ppm).

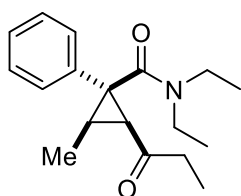


(1*R,2*S**,3*S**)-N,N-diethyl-2-methyl-1-phenyl-3-**

(trimethylsilyl)cyclopropane-1-carboxamide (77d)

Compound was obtained via [typical procedure C] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and chlorotrimethylsilane (57.0 μ L, 49.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by

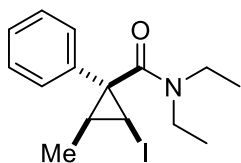
column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 72% yield (65.4 mg, 0.215 mmol). mp: 94.9-96.3 °C; R_f : 0.48; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.13 (m, 5H), 3.70 – 3.50 (m, 2H), 3.17 – 2.92 (m, 2H), 2.19 (dq, J = 10.6, 6.4 Hz, 1H), 1.17 (d, J = 6.5 Hz, 3H), 1.09 (t, J = 7.0 Hz, 3H), 0.48 (t, J = 7.1 Hz, 3H), 0.15 (s, 9H), -0.00 (d, J = 10.6 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.1, 144.0, 128.7 (+, 2C), 126.1 (+, 2C), 126.0 (+), 41.5 (-), 40.0, 39.2 (-), 26.1 (+), 21.9 (+), 13.6 (+), 12.8 (+), 12.7 (+), 1.3 (+, 3C); FTIR (KBr, cm^{-1}): 3053, 3007, 2970, 2945, 2895, 2874, 1627, 1599, 1462, 1444, 1427, 1373, 1261, 1240, 1155, 1101, 1053, 1022, 952, 858, 837, 802, 742, 702; HRMS (TOF ES): Found 326.1902, calculated for $\text{C}_{18}\text{H}_{29}\text{NOSiNa}$ ($\text{M}+\text{Na}$) 326.1916 (4.3 ppm).



(1*R,2*R**,3*S**)-N,N-diethyl-2-methyl-1-phenyl-3-propionylcyclopropane-1-carboxamide (77e)**

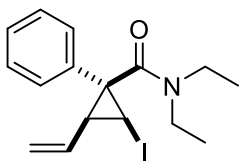
Compound was obtained via [typical procedure C] using Methylmagnesium bromide (135 μL , 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and propionyl chloride (40.0 μL , 42.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 79% yield (68.0 mg, 0.237 mmol). R_f : 0.23; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 3.41 (dq, J = 14.1, 7.1 Hz, 1H), 3.31 – 3.22 (m, 2H), 3.18 (dq, J = 14.1, 7.2 Hz, 1H), 2.79 (dq, J = 17.4, 7.4 Hz, 1H), 2.57 (dq, J = 17.3, 7.3 Hz, 1H), 2.29 (d, J = 9.0 Hz, 1H), 2.03 (dq, J = 8.9, 6.6 Hz, 1H), 1.49 (d, J = 6.6 Hz, 3H), 1.12 (t, J = 7.3 Hz, 3H), 1.10 (t, J = 7.1 Hz, 1H), 0.57 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 207.5, 167.3, 140.9, 129.0 (+, 2C), 127.1 (+), 126.4 (+, 2C), 43.7, 41.5 (-), 38.9 (-), 38.8 (-), 37.7 (+), 28.1 (+), 12.9 (+), 12.5 (+), 10.4 (+), 8.2 (+); FTIR (KBr, cm^{-1}): 3059, 2974, 2935, 2875, 1703, 1639,

1633, 1494, 1462, 1444, 1427, 1381, 1361, 1317, 1298, 1278, 1219, 1155, 1122, 1105, 1082, 1066, 1041, 904, 850, 833, 759, 700; HRMS (TOF ES): Found 310.1800, calculated for $C_{18}H_{25}NO_2Na$ (M+Na) 310.1783 (5.5 ppm).



(1*R,2*S**,3*S**)-N,N-diethyl-2-iodo-3-methyl-1-phenylcyclopropane-1-carboxamide (77f)**

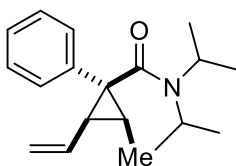
Compound was obtained via [typical procedure C] using Methylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and a saturated solution of diiodine in dry dimethoxyethane which was added until the coloration persisted. The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 63% yield (68.2 mg, 0.190 mmol). R_f : 0.45; dr: >99:1; 1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.19 (m, 5H), 3.56 – 3.46 (m, 1H), 3.50 (d, J = 6.9 Hz, 1H), 3.43 – 3.33 (m, 1H), 3.33 – 3.23 (m, 2H), 1.45 – 1.35 (m, 4H), 1.16 (t, J = 7.1 Hz, 3H), 0.58 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 140.4, 129.0 (+, 2C), 127.0 (+), 126.0 (+, 2C), 42.0 (-), 39.0 (-), 36.1, 26.5 (+), 18.1 (+), 12.6 (+), 12.6 (+), 7.2 (+); FTIR (KBr, cm^{-1}): 3057, 2970, 2931, 2872, 1633, 1599, 1496, 1444, 1425, 1379, 1315, 1296, 1278, 1263, 1234, 1219, 1149, 1122, 1103, 1080, 1066, 821, 761, 732; HRMS (TOF ES): Found 380.0474, calculated for $C_{15}H_{20}INONa$ (M+Na) 380.0487 (3.4 ppm).



(1*R,2*S**,3*S**)-N,N-diethyl-1-phenyl-2-propionyl-3-vinylcyclopropane-1-carboxamide (78aef)**

Compound was obtained via [typical procedure C] using vinylmagnesium bromide (405 μ L, 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.), N,N-diethyl-1-

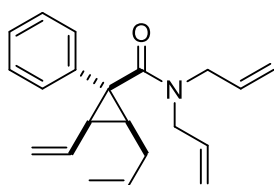
phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and a saturated solution of diiodine in dry dimethoxyethane which was added until coloration persisted. The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous light yellow oil in 51% yield (56.0 mg, 0.152 mmol). *R*_f: 0.52; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.19 (m, 5H), 5.89 – 5.68 (m, 1H), 5.37 – 5.21 (m, 2H), 3.56 (d, *J* = 8.4 Hz, 1H), 3.52 – 3.41 (m, 1H), 3.36 – 3.24 (m, 2H), 3.21 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.19 – 1.94 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.54 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.7, 139.4, 138.7 (+), 129.1 (+, 2C), 127.4 (+), 126.0 (+, 2C), 117.5 (-), 42.0 (-), 39.2 (-), 38.8, 35.2 (+), 12.6 (+), 12.5 (+), 4.0 (+); FTIR (KBr, cm⁻¹): 3080, 3057, 3020, 2972, 2933, 2872, 1631, 1494, 1471, 1458, 1429, 1379, 1313, 1296, 1278, 1257, 1219, 1141, 1101, 1078, 979, 964, 904, 761, 700; HRMS (TOF ES): Found 369.0601, calculated for C₁₆H₂₀INO (M⁺) 369.0590 (3.0 ppm).



(1*S,2*S**,3*R**)-N,N-diisopropyl-2-methyl-1-phenyl-3-vinylcyclopropane-1-carboxamide (**78bea**)**

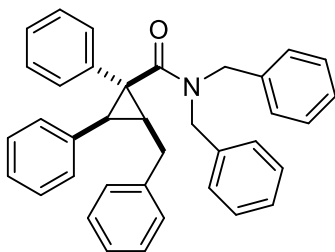
Compound was obtained via [typical procedure C] using vinylmagnesium bromide (405 μL, 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.), N,N-diisopropyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ab**) (73.0 mg, 0.30 mmol, 1.0 equiv.), and methyl iodide (28.0 μL, 64.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a yellow solid in 81% yield (69.4 mg, 0.243 mmol). mp: 94.4-96.0 °C; *R*_f: 0.61; dr: >99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.27 (m, 4H), 7.22 – 7.15 (m, 1H), 5.95 – 5.74 (m, 1H), 5.22 (d, *J* = 17.0 Hz, 1H), 5.13 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.14 (hept, *J* = 6.6 Hz, 1H), 3.19 (hept, *J* = 6.8 Hz, 1H), 2.08 (s (broad), 1H), 1.76 (s (broad), 1H), 1.42 (t, *J* = 6.5 Hz, 6H), 1.33 (d, *J* = 6.6 Hz,

3H), 0.78 (s (broad), 3H), 0.64 (s (broad), 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.3, 142.0, 135.1 (+), 128.7 (+, 2C), 126.4 (+), 126.2 (+, 2C), 115.8 (-, broad), 48.9 (+), 45.8 (+), 40.8 (broad), 35.0 (+, broad), 26.2 (+, broad), 20.8 (+), 20.6 (+), 20.4 (+), 20.1 (+), 11.4 (+); FTIR (KBr, cm^{-1}): 3080, 3059, 3001, 2962, 2929, 2872, 1633, 1494, 1435, 1369, 1336, 1211, 1155, 1118, 1039, 987, 900, 734; HRMS (TOF ES): Found 286.2162, calculated for $\text{C}_{19}\text{H}_{28}\text{NO}$ ($\text{M}+\text{H}$) 286.2171 (3.1 ppm).



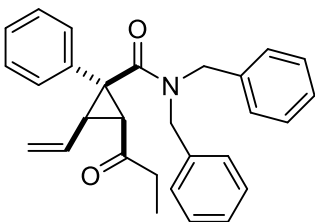
(1*S,2*S**,3*R**)-N,N,2-triallyl-1-phenyl-3-vinylcyclopropane-1-carboxamide (78ceb)**

Compound was obtained via [typical procedure C] using vinylmagnesium bromide (405 μL , 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.), N,N-diallyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ac**) (72.0 mg, 0.30 mmol, 1.0 equiv.), and allyl bromide (39.0 μL , 55.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 76% yield (70.2 mg, 0.228 mmol). R_f : 0.45; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.15 (m, 5H), 6.09 – 5.88 (m, 1H), 5.82 – 5.63 (m, 2H), 5.34 (dd, J = 16.9, 1.7 Hz, 1H), 5.18 (dd, J = 10.3, 1.8 Hz, 1H), 5.13 (dd, J = 10.2, 1.4 Hz, 1H), 5.09 (dd, J = 17.2, 1.6 Hz, 2H), 5.00 (dd, J = 10.3, 1.9 Hz, 1H), 4.94 – 4.90 (m, 3H), 4.11 – 3.97 (m, 1H), 3.94 – 3.66 (m, 3H), 2.81 – 2.65 (m, 1H), 2.48 – 2.35 (m, 1H), 2.33 – 2.18 (m, 1H), 1.61 – 1.50 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.0, 141.2, 137.4 (+), 133.7 (+), 133.4 (+), 132.9 (+), 128.9 (+, 2C), 126.7 (+), 126.0 (+, 2C), 118.7 (-), 117.8 (-), 117.2 (-), 115.3 (-), 50.0 (-), 46.0 (-), 38.8, 33.3 (+), 32.9 (+), 30.6 (-); FTIR (KBr, cm^{-1}): 3078, 3003, 2980, 2920, 1643, 1631, 1600, 1496, 1450, 1435, 1410, 1330, 1298, 1282, 1269, 1205, 1192, 1128, 993, 922, 910, 759, 734; HRMS (TOF ES): Found 330.1822, calculated for $\text{C}_{21}\text{H}_{25}\text{NONa}$ ($\text{M}+\text{Na}$) 330.1834 (3.6 ppm).



(1*S,2*S**,3*S**)-N,N,2-tribenzyl-1,3-diphenylcyclopropane-1-carboxamide (78ddc)**

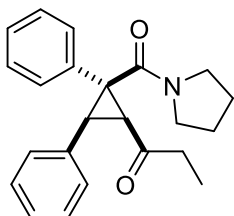
Compound was obtained via [typical procedure C] using phenylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), N,N-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ad**) (102 mg, 0.30 mmol, 1.0 equiv.), and benzyl bromide (54.0 μ L, 77.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 9:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 79% yield (120 mg, 0.236 mmol). mp: 143.5-146.1 $^{\circ}$ C; R_f : 0.38; dr: 15:1; ^1H NMR (500 MHz, CDCl_3) δ 7.58 – 7.47 (m, 2H), 7.40 – 6.87 (m, 21H), 6.28 – 6.12 (m, 2H), 4.95 (d, J = 14.0 Hz, 1H), 4.73 (d, J = 15.6 Hz, 1H), 3.80 (dd, J = 15.2, 4.9 Hz, 1H), 3.78 (d, J = 14.0 Hz, 1H), 3.68 (d, J = 15.6 Hz, 1H), 3.20 (d, J = 9.9 Hz, 1H), 2.99 (dd, J = 15.2, 9.0 Hz, 1H), 1.67 (ddd, J = 9.9, 9.0, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.0, 142.2, 142.1, 136.6, 136.6, 135.6, 130.0 (+, 2C), 129.1 (+, 2C), 128.8 (+, 2C), 128.7 (+, 2C), 128.5 (+, 2C), 128.3 (+, 2C), 128.3 (+, 2C), 128.2 (+, 2C), 127.9 (+, 2C), 127.5 (+), 127.3 (+, 2C), 127.2 (+), 127.0 (+), 126.3 (+), 125.7 (+), 50.3 (-), 46.8 (-), 39.3, 36.8 (+), 32.3 (+), 30.5 (-); FTIR (KBr, cm^{-1}): 3084, 3061, 3028, 2929, 2914, 2862, 1952, 1880, 1809, 1643, 1633, 1600, 1494, 1454, 1417, 1361, 1329, 1265, 1209, 1078, 1030, 1003, 958, 943, 916, 842, 823, 767, 732, 700; HRMS (TOF ES): Found 530.2451, calculated for $\text{C}_{37}\text{H}_{33}\text{NONa}$ ($\text{M}+\text{Na}$) 530.2460 (1.7 ppm).



(1*R,2*S**,3*R**)-N,N-dibenzyl-1-phenyl-2-propionyl-3-vinylcyclopropane-1-carboxamide (78dee)**

Compound was obtained via [typical procedure C] using vinylmagnesium bromide (405 μ L, 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.), N,N-dibenzyl-1-phenylcycloprop-2-ene-1-carboxamide (**53ad**) (102 mg, 0.30

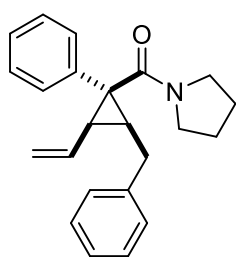
mmol, 1.0 equiv.), and propionyl chloride (40.0 μ L, 42.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 9:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 52% yield (66.1 mg, 0.156 mmol). R_f : 0.19; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.50 – 7.41 (m, 2H), 7.34 – 7.20 (m, 6H), 7.17 – 7.03 (m, 5H), 6.57 – 6.46 (m, 1H), 6.48 – 6.44 (m, 2H), 5.32 (dd, J = 17.2, 1.8 Hz, 1H), 5.13 (dd, J = 10.3, 1.8 Hz, 1H), 4.82 (d, J = 14.6 Hz, 1H), 4.52 (d, J = 15.5 Hz, 1H), 4.14 (d, J = 15.5 Hz, 1H), 3.95 (d, J = 14.6 Hz, 1H), 2.92 – 2.80 (m, 1H), 2.78 – 2.70 (m, 1H), 2.70 – 2.57 (m, 2H), 1.18 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 206.8, 167.8, 139.6, 136.8, 135.6, 132.8 (+), 129.2 (+, 2C), 129.0 (+, 2C), 128.4 (+, 2C), 128.4 (+, 2C), 127.9 (+, 2C), 127.8 (+), 127.5 (+, 2C), 127.4 (+), 127.4 (+), 117.6 (-), 50.2 (-), 46.7 (-), 45.7, 39.3 (+), 38.9 (-), 37.6 (+), 8.2 (+); FTIR (KBr, cm^{-1}): 3061, 3028, 3003, 2978, 2935, 1707, 1643, 1633, 1602, 1494, 1450, 1417, 1361, 1329, 1315, 1267, 1234, 1193, 1178, 1122, 1080, 1039, 1030, 989, 945, 908, 806, 734, 700; HRMS (TOF ES): Found 446.2100, calculated for $\text{C}_{29}\text{H}_{29}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) 446.2096 (0.9 ppm).



1-((1S*,2R*,3S*)-2,3-diphenyl-2-(pyrrolidin-1-carbonyl)cyclopropyl)propan-1-one (78ide)

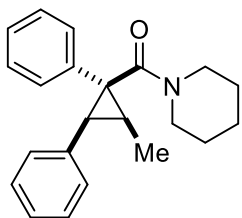
Compound was obtained via [typical procedure C] using phenylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (**53ai**) (64.0 mg, 0.30 mmol, 1.0 equiv.), and propionyl chloride (40.0 μ L, 42.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 80% yield (83.1 mg, 0.239 mmol). mp: 112.1–114.2 $^{\circ}\text{C}$; R_f : 0.18; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.54 – 7.14 (m, 10H), 3.41 – 3.26 (m, 2H), 3.12 (d, J = 9.3 Hz, 1H), 3.12 – 3.05 (m, 1H), 2.85 – 2.74 (m, 1H), 2.68 – 2.53 (m, 2H), 2.36 (d, J = 9.3 Hz,

1H), 1.58 – 1.49 (m, 2H), 1.48 – 1.39 (m, 1H), 1.16 (t, $J = 7.3$ Hz, 3H), 1.06 – 0.95 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 205.7, 166.4, 140.1, 134.1, 129.8 (+, 2C), 129.1 (+, 2C), 127.6 (+, 2C), 127.4 (+), 126.8 (+), 126.6 (+, 2C), 46.9 (-), 46.3, 46.2 (-), 40.8 (+), 38.4 (-), 35.4 (+), 25.7 (-), 23.9 (-), 8.3 (+); FTIR (KBr, cm^{-1}): 3057, 3028, 2974, 2947, 2875, 1712, 1631, 1579, 1496, 1448, 1431, 1373, 1340, 1265, 1251, 1224, 1190, 1168, 1128, 1095, 1080, 1033, 962, 914, 869, 842, 771, 732, 700; HRMS (TOF ES): Found 370.1771, calculated for $\text{C}_{23}\text{H}_{25}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) 370.1783 (3.2 ppm).



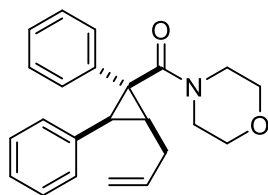
((1*S,2*S**,3*R**)-2-benzyl-1-phenyl-3-vinylcyclopropyl)(pyrrolidin-1-yl)methanone (78iec)**

Compound was obtained via [typical procedure C] using vinylmagnesium bromide (405 μL , 1.0 M (tetrahydrofuran), 0.405 mmol, 1.35 equiv.), (1-phenylcycloprop-2-en-1-yl)(pyrrolidin-1-yl)methanone (**53ai**) (64.0 mg, 0.30 mmol, 1.0 equiv.), and benzyl bromide (54.0 μL , 77.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 79% yield (78.2 mg, 0.236 mmol). R_f : 0.26; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.14 (m, 10H), 5.98 – 5.70 (m, 1H), 5.37 (dd, $J = 17.0$, 1.8 Hz, 1H), 5.20 (dd, $J = 10.3$, 1.8 Hz, 1H), 3.62 – 3.48 (m, 2H), 3.45 (dd, $J = 15.3$, 5.2 Hz, 1H), 3.35 – 3.23 (m, 1H), 2.96 – 2.85 (m, 2H), 2.50 (dd, $J = 10.2$, 9.2 Hz, 1H), 1.85 – 1.71 (m, 2H), 1.71 – 1.61 (m, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.2, 141.9, 140.9, 133.9 (+), 128.9 (+, 2C), 128.8 (+, 2C), 128.4 (+, 2C), 126.5 (+), 125.9 (+), 125.6 (+, 2C), 117.4 (-), 46.8 (-), 46.1 (-), 40.0, 36.1 (+), 33.1 (+), 32.1 (-), 26.3 (-), 24.1 (-); FTIR (KBr, cm^{-1}): 3082, 3059, 3024, 2972, 2874, 1633, 1600, 1494, 1450, 1419, 1340, 1249, 1222, 1190, 1170, 1124, 1112, 1080, 1031, 983, 910, 758, 736; HRMS (TOF ES): Found 354.1834, calculated for $\text{C}_{23}\text{H}_{25}\text{NONa}$ ($\text{M}+\text{Na}$) 354.1834 (3.1 ppm).



((1*S,2*S**,3*S**)-2-methyl-1,3-diphenylcyclopropyl)(piperidin-1-yl)methanone (78jda)**

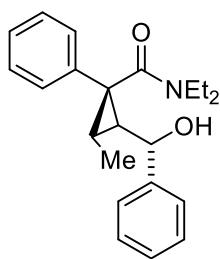
Compound was obtained via [typical procedure C] using phenylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aj**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and methyl iodide (28.0 μ L, 64.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 87% yield (83.4 mg, 0.261 mmol). mp: 121.1–125.4 $^{\circ}$ C; R_f : 0.42; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.32 (m, 4H), 7.30 – 7.27 (m, 4H), 7.24 – 7.19 (m, 2H), 3.58 – 3.46 (m, 2H), 3.11 – 2.98 (m, 1H), 2.89 (d, J = 10.0 Hz, 1H), 2.87 – 2.82 (m, 1H), 1.68 (dq, J = 9.9, 6.7 Hz, 1H), 1.48 (d, J = 6.8 Hz, 3H), 1.44 – 1.34 (m, 2H), 1.34 – 1.23 (m, 2H), 0.87 – 0.73 (m, 1H), 0.51 – 0.39 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.8, 142.5, 136.9, 129.4 (+, 2C), 128.8 (+, 2C), 127.9 (+, 2C), 126.4 (+), 126.2 (+), 125.6 (+, 2C), 46.7 (-), 42.3 (-), 38.3, 34.8 (+), 30.3 (+), 25.1 (-), 24.8 (-), 24.3 (-), 10.0 (+); FTIR (KBr, cm^{-1}): 3057, 3026, 2935, 2854, 1631, 1496, 1435, 1384, 1367, 1352, 1294, 1276, 1251, 1219, 1199, 1126, 1060, 1031, 1001, 852, 763, 744, 727, 700; HRMS (TOF ES): Found 342.1845, calculated for $\text{C}_{22}\text{H}_{25}\text{NONa}$ ($\text{M}+\text{Na}$) 342.1834 (3.2 ppm).



((1*S,2*S**,3*S**)-2-allyl-1,3-diphenylcyclopropyl)(morpholino)methanone (78kdb)**

Compound was obtained via [typical procedure C] using phenylmagnesium bromide (135 μ L, 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.), morpholino(1-phenylcycloprop-2-en-1-yl)methanone (**53ak**) (69.0 mg, 0.30 mmol, 1.0 equiv.), and allyl bromide (39.0 μ L, 55.0 mg, 0.45 mmol, 1.50 equiv.). The product was purified by column

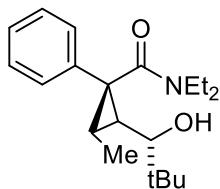
chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 87% yield (91.2 mg, 0.262 mmol). mp: 102.4-103.5 °C; R_f : 0.29; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.45 – 7.18 (m, 10H), 5.95 – 5.69 (m, 1H), 4.96 (dd, J = 17.2, 1.9 Hz, 1H), 4.88 (dd, J = 10.2, 1.9 Hz, 1H), 3.80 – 3.66 (m, 1H), 3.58 – 3.49 (m, 1H), 3.48 – 3.33 (m, 2H), 3.10 – 2.87 (m, 4H), 3.03 (d, J = 9.9 Hz, 1H), 2.60 – 2.46 (m, 1H), 2.44 – 2.31 (m, 1H), 1.59 – 1.39 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.8, 141.5, 137.6 (+), 136.4, 128.9 (+, 2C), 128.7 (+, 2C), 128.2 (+, 2C), 126.7 (+), 126.6 (+), 125.5 (+, 2C), 114.9 (-), 66.0 (-), 65.4 (-), 46.1 (-), 41.7 (-), 38.4, 35.9 (+), 33.3 (+), 28.7 (-); FTIR (KBr, cm^{-1}): 3059, 3028, 3001, 2970, 2920, 2899, 2856, 1639, 1600, 1498, 1456, 1427, 1359, 1300, 1273, 1222, 1192, 1114, 1070, 1030, 999, 968, 912, 839; HRMS (TOF ES): Found 370.1765, calculated for $\text{C}_{23}\text{H}_{25}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) 370.1783 (4.9 ppm).



(1*R,2*R**,3*S**)-N,N-diethyl-2-((*R**)-hydroxy(phenyl)methyl)-3-methyl-1-phenylcyclopropane-1-carboxamide (83aa)**

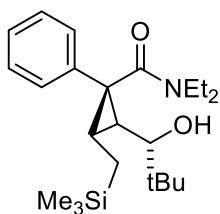
Compound was obtained via [Typical Procedure D] using methylmagnesium bromide (130 μL , 3.0 M (tetrahydrofuran), 0.40 mmol, 1.30 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and a freshly distilled benzaldehyde (48.0 mg, 46.0 μL , 0.45 mmol, 1.5 equiv.). The product was purified by column chromatography using silica and a 2:1 hexane:diethyl ether mobile phase. The titled compound was obtained as colorless solid in 60% yield (60.9 mg, 0.180 mmol). mp: 140.9-143.6 °C; R_f : 0.31; dr: 92:8; ^1H NMR (500 MHz, CDCl_3) δ 7.48 – 7.42 (m, 2H), 7.35 – 7.27 (m, 4H), 7.26 – 7.16 (m, 4H), 5.81 (s, 1H), 4.78 (d, J = 10.3 Hz, 1H), 3.72 – 3.59 (m, 2H), 3.27 – 3.12 (m, 2H), 2.12 (dq, J = 9.6, 6.6 Hz, 1H), 1.42 (dd, J = 10.4, 9.6 Hz, 1H), 1.34 (d, J = 6.6 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H), 0.60 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.7, 143.8, 141.4, 128.9 (+, 2C), 128.5

(+, 2C), 127.3 (+), 126.7 (+), 126.3 (+, 2C), 126.2 (+, 2C), 70.8 (+), 42.2 (+), 41.9 (-), 39.2 (-), 38.6, 20.7 (+), 12.8 (+), 12.6 (+), 10.6 (+); FTIR (KBr, cm^{-1}): 3358, 2972, 2935, 2875, 1608, 1495, 1422, 1380, 1347, 1318, 1252, 1155, 699; HRMS (TOF ES): Found 360.1949, calculated for $\text{C}_{22}\text{H}_{27}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) 360.1939 (2.8 ppm).



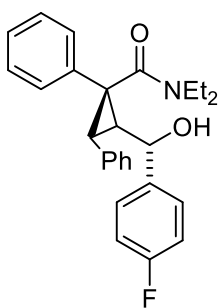
(1*R,2*R**,3*S**)-N,N-diethyl-2-((*R**)-1-hydroxy-2,2-dimethylpropyl)-3-methyl-1-phenylcyclopropane-1-carboxamide (83ac)**

Compound was obtained via [typical procedure D] using methylmagnesium bromide (130.0 μL , 3.0 M (tetrahydrofuran), 0.390 mmol, 1.30 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and freshly distilled pivaldehyde (38.8 mg, 48.9 μL , 0.450 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 2:1 hexane:diethyl ether mobile phase. The titled compound was obtained as colorless solid in 79% yield (75.1 mg, 0.237 mmol). mp: 138.1 – 139.4 $^{\circ}\text{C}$; R_f : 0.36; dr: >98:2; ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.29 (m, 2H), 7.27 – 7.19 (m, 3H), 5.79 (d, J = 2.3 Hz, 1H), 3.73 – 3.60 (m, 2H), 3.41 (dd, J = 10.5, 2.3 Hz, 1H), 3.18 – 3.06 (m, 2H), 2.10 (dq, J = 9.6, 6.6 Hz, 1H), 1.21 (d, J = 6.6 Hz, 3H), 1.20 – 1.16 (m, 1H), 1.15 (t, J = 7.1 Hz, 3H), 0.99 (s, 9H), 0.52 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.0, 142.1, 128.9 (+, 2C), 126.5 (+), 126.2 (+, 2C), 74.8 (+), 41.8 (-), 39.1 (-), 38.0 (+), 36.9, 35.0, 26.3 (+, 3C), 21.3 (+), 12.5 (+), 12.4 (+), 11.1 (+); FTIR (KBr, cm^{-1}): 3348, 3027, 2968, 2873, 1604, 1460, 1429, 1063, 1007, 702; HRMS (TOF ES): Found 340.2255, calculated for $\text{C}_{20}\text{H}_{31}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) 340.2252 (0.9 ppm).



(1*S,2*R**,3*R**)-N,N-diethyl-2-((*R**)-1-hydroxy-2,2-dimethylpropyl)-1-phenyl-3-((trimethylsilyl)methyl)cyclopropane-1-carboxamide (83cc)**

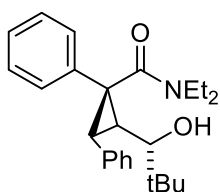
Compound was obtained via [typical procedure D] using (trimethylsilyl)methylmagnesium chloride (450 μ L, 1.3 M (tetrahydrofuran), 0.60 mmol, 1.30 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (98.0 mg, 0.45 mmol, 1.0 equiv.), and freshly distilled pivaldehyde (59.0 mg, 75.0 μ L, 0.68 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 2:1 hexane:diethyl ether mobile phase. The titled compound was obtained as colorless oil in 79% yield (138 mg, 0.354 mmol). *R*_f: 0.45; dr: > 99:1; ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 3.61 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.57 – 3.48 (m, 1H), 3.48 (d, *J* = 10.0 Hz, 1H), 3.14 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.97 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.14 – 1.09 (m, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.96 (s, 9H), 0.88 (dd, *J* = 15.7, 5.2 Hz, 1H), 0.43 (t, *J* = 7.1 Hz, 3H), 0.43 – 0.38 (m, 1H), 0.12 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 171.2, 142.4, 129.0 (+, 2C), 126.5 (+), 126.4 (+, 2C), 74.6 (+), 42.0 (-), 39.3 (-), 38.6 (+), 38.5, 35.5, 26.5 (+, 3C), 20.9 (+), 12.5 (+), 12.3 (+), 10.2 (-), -1.1 (+, 3C); FTIR (KBr, cm⁻¹): 3365, 2951, 2901, 1614, 1479, 1462, 1445, 1249, 1184, 1064, 846, 698; HRMS (TOF ES): Found 412.2644, calculated for C₂₃H₃₉NO₂SiNa (M+Na) 412.2648 (1.0 ppm).



(1*R,2*R**,3*R**)-N,N-diethyl-2-((*R**)-(4-fluorophenyl)(hydroxy)methyl)-1,3-diphenylcyclopropane-1-carboxamide (**83db**)**

Compound was obtained via [Typical Procedure D] using phenylmagnesium bromide (130 μ L, 3.0 M (tetrahydrofuran), 0.40 mmol, 1.30 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and a 4-fluorobenzaldehyde (58.0 mg, 50.0 μ L, 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 2:1 hexane:diethyl ether mobile phase. The titled compound was obtained as colorless oil in 88% yield (110 mg, 0.263 mmol). *R*_f: 0.31; dr: 93:7; ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.39 (m, 2H), 7.38 – 7.33 (m, 4H),

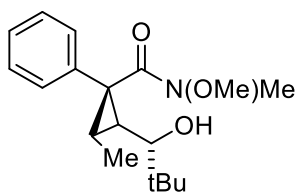
7.31 – 7.22 (m, 4H), 6.96 – 6.88 (m, 2H), 6.85 – 6.77 (m, 2H), 5.98 (s, 1H), 5.16 (d, $J = 10.4$ Hz, 1H), 3.58 (dq, $J = 14.1, 7.2$ Hz, 1H), 3.36 (dq, $J = 14.4, 7.1$ Hz, 1H), 3.30 – 3.21 (m, 1H), 3.19 (d, $J = 10.0$ Hz, 1H), 2.75 (dq, $J = 14.1, 7.0$ Hz, 1H), 1.65 (t, $J = 10.2$ Hz, 1H), 1.18 (t, $J = 7.1$ Hz, 3H), 0.33 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.2, 161.8 (d, $J = 244.3$ Hz), 141.0, 139.1 (d, $J = 3.5$ Hz), 136.0, 128.9 (d, $J = 24.4$ Hz, +, 2C), 128.4 (+, 2C), 127.2 (d, $J = 8.1$ Hz, +, 2C), 127.1 (+, 2C), 126.9 (+, 2C), 126.3 (+, 2C), 114.8 (+), 114.7 (+), 68.1 (+), 43.9 (+), 41.9 (-), 40.6, 39.4 (-), 32.2 (+), 11.9 (+), 11.8 (+); ^{19}F NMR (376 MHz, CDCl_3) δ -116.3 (s, 1F); FTIR (KBr, cm^{-1}): 3354, 2976, 2924, 1606, 1509, 1458, 1381, 1314, 1154, 1033, 767, 700; HRMS (TOF ES): Found 440.1987, calculated for $\text{C}_{27}\text{H}_{28}\text{FNO}_2\text{Na}$ ($\text{M}+\text{Na}$) 440.2002 (3.4 ppm).



(1*R,2*R**,3*R**)-N,N-diethyl-2-((*R**)-1-hydroxy-2,2-dimethylpropyl)-1,3-diphenylcyclopropane-1-carboxamide (83dc)**

Compound was obtained via [Typical Procedure D] using phenylmagnesium bromide (130 μL , 3.0 M (tetrahydrofuran), 0.40 mmol, 1.30 equiv.), N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.), and freshly distilled pivaldehyde (39.0 mg, 50.0 μL , 0.45 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 2:1 hexane:diethyl ether mobile phase. The titled compound was obtained as colorless solid in 83% yield (94.2 mg, 0.248 mmol). A 4X times scale (1.2 mmol) resulted in 85% yield. (388 mg, 1.02 mmol). mp: 196.9 – 198.0 $^{\circ}\text{C}$; R_f : 0.38; dr: >99:1; ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.39 (m, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.19 (m, 6H), 3.85 (d, $J = 10.7$ Hz, 1H), 3.52 (dq, $J = 14.1, 7.2$ Hz, 1H), 3.25 (dq, $J = 14.3, 7.2$ Hz, 1H), 3.19 – 3.10 (m, 1H), 3.13 (d, $J = 9.9$ Hz, 1H), 2.61 (dq, $J = 14.2, 7.1$ Hz, 1H), 1.65 (s, 1H), 1.53 (t, $J = 10.4$ Hz, 1H), 1.10 (t, $J = 7.1$ Hz, 3H), 0.73 (s, 9H), 0.25 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.5, 141.9, 137.1, 129.1 (+, 2C), 129.0 (+, 2C), 128.2 (+, 2C), 126.9 (+), 126.5 (+), 126.5 (+, 2C), 72.7 (+), 41.8

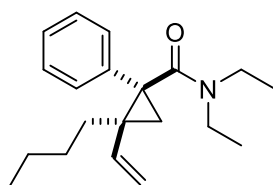
(-), 39.3 (-), 39.1 (+), 39.0, 35.3, 33.5 (+), 26.2 (+, 3C), 12.0 (+), 11.9 (+); FTIR (KBr, cm^{-1}): 3363, 2964, 2648, 1595, 1463, 1442, 1433, 1007, 765, 699; HRMS (TOF ES): Found 402.2411, calculated for $\text{C}_{25}\text{H}_{33}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) 402.2409 (0.5 ppm).



(1*R,2*R**,3*S**)-2-((*R**)-1-hydroxy-2,2-dimethylpropyl)-N-methoxy-N,3-dimethyl-1-phenylcyclopropane-1-carboxamide**
(84)

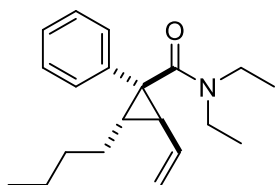
Compound was obtained via [typical procedure D] using methylmagnesium bromide (260 μL , 3.0 M (tetrahydrofuran), 0.780 mmol, 1.30 equiv.), N-methoxy-N-methyl-1-phenylcycloprop-2-ene-1-carboxamide (**53au**) (122.0 mg, 0.60 mmol, 1.0 equiv.), and freshly distilled pivaldehyde (77.6 mg, 98.0 μL , 0.90 mmol, 1.50 equiv.). The product was purified by column chromatography using silica and a 2:1 hexane:diethyl ether mobile phase. The titled compound was obtained as colorless oil in 82% yield (151 mg, 0.494 mmol). R_f : 0.30; dr: >98:2; ^1H NMR (500 MHz, CDCl_3): ^1H NMR (500 MHz, C_6D_6) δ 7.25 – 7.19 (m, 2H), 7.10 – 7.03 (m, 2H), 7.01 – 6.95 (m, 1H), 5.36 (s, 1H), 3.61 (d, J = 10.4 Hz, 1H), 2.77 (s, 3H), 2.75 (s, 3H), 1.93 – 1.81 (m, 1H), 1.30 (t, J = 9.9 Hz, 1H), 1.15 (d, J = 6.7 Hz, 3H), 1.11 (s, 9H); ^{13}C NMR (126 MHz, C_6D_6) δ 172.8, 142.7, 128.8 (+, 2C), 127.5 (+), 126.6 (+, 2C), 74.9 (+), 59.9 (+), 38.0 (+), 37.7, 35.4, 33.0 (+), 26.6 (+, 3C), 22.2 (+), 10.9 (+); FTIR (KBr, cm^{-1}): 3416, 3061, 2953, 2905, 1631, 1460, 1380, 1178, 1007, 699, 611; HRMS (TOF ES): Found 328.1885, calculated for $\text{C}_{18}\text{H}_{27}\text{NO}_3\text{Na}$ ($\text{M}+\text{Na}$) 328.1889 (1.2 ppm).

3.13.4 Carbomagnesiation of Substituted Cyclopropenes



(1*S,2*S**)-2-butyl-N,N-diethyl-1-phenyl-2-vinylcyclopropane-1-carboxamide (93be)**

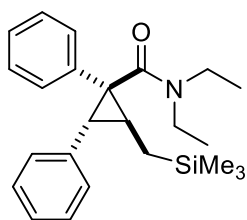
Compound was obtained via [typical procedure A] using vinylmagnesium bromide (390 μ L, 1.0 M (tetrahydrofuran), 0.390 mmol, 1.30 equiv.) and 2-butyl-N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (82.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless oil in 88% yield (78.7 mg, 0.263 mmol). R_f : 0.30; Rs: 81:19 (Geminal Product Major); dr: >98:2; ^1H NMR (500 MHz, CDCl_3) δ 7.49 – 7.43 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 5.94 (dd, J = 17.2, 10.5 Hz, 1H), 5.05 (dd, J = 10.5, 1.4 Hz, 1H), 4.98 (dd, J = 17.2, 1.4 Hz, 1H), 3.56 (dq, J = 14.2, 7.1 Hz, 1H), 3.36 (dq, J = 14.2, 7.1 Hz, 1H), 3.27 (dq, J = 14.1, 7.1 Hz, 1H), 3.17 (dq, J = 13.9, 7.1 Hz, 1H), 1.62 (d, J = 5.3 Hz, 1H), 1.61 – 1.51 (m, 1H), 1.36 (d, J = 5.2 Hz, 1H), 1.34 – 1.28 (m, 1H), 1.24 – 1.02 (m, 3H), 0.97 (t, J = 7.1 Hz, 3H), 0.83 (t, J = 7.1 Hz, 3H), 0.81 – 0.76 (m, 1H), 0.74 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.1, 141.1 (+), 137.8, 129.7 (+, 2C), 128.4 (+, 2C), 126.9 (+), 113.1 (-), 42.3, 41.6 (-), 39.2 (-), 35.4, 32.8 (-), 29.0 (-), 22.8 (-), 21.7 (-), 14.1 (+), 13.7 (+), 12.6 (+); FTIR (KBr, cm^{-1}): 3052, 2958, 2932, 2871, 1633, 1458, 1424, 1275, 1100, 902, 701; HRMS (TOF ES): Found 322.2157, calculated for $\text{C}_{20}\text{H}_{29}\text{NONa}$ ($\text{M}+\text{Na}$) 322.2147 (3.1 ppm).



(1*R,2*S**,3*S**)-2-butyl-N,N-diethyl-1-phenyl-3-vinylcyclopropane-1-carboxamide (94be)**

R_f : 0.40; dr: >98:2; ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.26 (m, 4H), 7.24 – 7.19 (m, 1H), 5.47 – 5.35 (m, 1H), 5.26 (dd, J = 17.0, 1.8 Hz, 1H), 5.01 (dd, J = 10.1, 1.8 Hz, 1H),

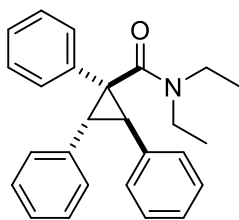
3.61 – 3.44 (m, 2H), 3.06 (dq, $J = 13.8, 7.0$ Hz, 1H), 2.89 (dq, $J = 14.1, 7.0$ Hz, 1H), 2.26 (dd, $J = 9.2, 6.0$ Hz, 1H), 2.05 – 1.88 (m, 1H), 1.35 – 1.07 (m, 6H), 1.04 (t, $J = 7.1$ Hz, 3H), 0.75 (t, $J = 7.2$ Hz, 3H), 0.34 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.5, 137.6, 137.0 (+), 128.6 (+, 2C), 128.4 (+, 2C), 126.7 (+), 115.2 (-), 42.7, 41.1 (-), 39.6 (-), 32.4 (+), 31.5 (+), 31.0 (-), 28.2 (-), 22.4 (-), 14.1 (+), 12.4 (+), 12.4 (+).



(1*R,2*R**,3*S**)-N,N-diethyl-1,2-diphenyl-3-**

((trimethylsilyl)methyl)cyclopropane-1-carboxamide (94ac)

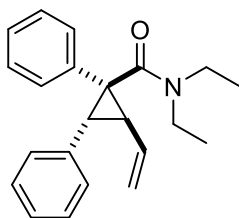
Compound was obtained via [typical procedure A] using (trimethylsilyl)methylmagnesium chloride (300 μL , 1.3 M (tetrahydrofuran), 0.390 mmol, 1.3 equiv.) and N,N-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**53aa**) (88.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 70% yield (79.4 mg, 0.209 mmol). mp: 186.8 – 187.4 $^{\circ}\text{C}$; R_f : 0.30; Rs: >98:2; dr: >98:2; ^1H NMR (500 MHz, CDCl_3) δ 7.07 (d, $J = 4.3$ Hz, 4H), 7.04 – 6.90 (m, 6H), 3.71 (dq, $J = 14.3, 7.1$ Hz, 1H), 3.54 (dq, $J = 13.9, 7.1$ Hz, 1H), 3.18 (dq, $J = 13.9, 7.0$ Hz, 1H), 3.05 (dq, $J = 14.0, 7.0$ Hz, 1H), 2.98 (d, $J = 6.8$ Hz, 1H), 2.35 (ddd, $J = 12.3, 6.8, 2.7$ Hz, 1H), 1.12 (t, $J = 7.1$ Hz, 3H), 1.05 (dd, $J = 14.4, 2.7$ Hz, 1H), 0.41 – 0.35 (m, 1H), 0.38 (t, $J = 7.1$ Hz, 3H), 0.09 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.5, 137.5, 137.3, 128.9 (+, 2C), 128.5 (+, 2C), 128.1 (+, 2C), 127.6 (+, 2C), 126.3 (+), 125.6 (+), 45.0, 41.5 (-), 39.8 (-), 37.1 (+), 22.7 (+), 16.4 (-), 12.7 (+), 12.5 (+), -1.2 (+, 3C); FTIR (KBr, cm^{-1}): 3056, 2956, 2902, 1622, 1443, 1426, 1250, 858, 832, 696; HRMS (TOF ES): Found 402.2226, calculated for $\text{C}_{24}\text{H}_{33}\text{NOSiNa}$ ($\text{M}+\text{Na}$) 402.2229 (0.7 ppm).



(2*R,3*R**)-N,N-diethyl-1,2,3-triphenylcyclopropane-1-carboxamide**

(94ad)

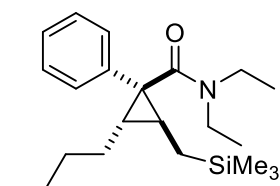
Compound was obtained via [typical procedure A] using phenylmagnesium bromide (130.0 μ L, 3.0 M (diethyl ether), 0.390 mmol, 1.30 equiv.) and N,N-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**53aa**) (88.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 89% yield (99.2 mg, 0.268 mmol). mp: 174.3 – 175.6 °C; R_f : 0.27; Rs: >98:2; dr: >98:2; ^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.20 (m, 3H), 7.17 – 7.12 (m, 2H), 7.11 – 7.03 (m, 5H), 7.02 – 6.97 (m, 1H), 3.90 (d, J = 7.3 Hz, 1H), 3.55 (d, J = 7.3 Hz, 1H), 3.51 – 3.31 (m, 2H), 2.77 (dq, J = 13.9, 7.0 Hz, 1H), 2.48 (dq, J = 14.1, 7.0 Hz, 1H), 0.69 (t, J = 7.1 Hz, 3H), 0.17 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.7, 136.9, 136.8, 136.6, 128.8 (+, 2C), 128.6 (+, 2C), 128.4 (+, 2C), 128.3 (+, 2C), 127.8 (+, 2C), 127.7 (+, 2C), 126.8 (+), 126.7 (+), 126.1 (+), 48.6, 41.0 (-), 39.2 (-), 35.2 (+), 32.5 (+), 12.0 (+), 11.8 (+); FTIR (KBr, cm^{-1}): 3046, 3029, 2974, 2934, 1624, 1446, 1277, 1078, 774, 750, 697; HRMS (TOF ES): Found 392.1982, calculated for $\text{C}_{26}\text{H}_{27}\text{NONa}$ ($\text{M}+\text{Na}$) 392.1990 (2.0 ppm).



(1*S,2*R**,3*S**)-N,N-diethyl-1,2-diphenyl-3-vinylcyclopropane-1-carboxamide (94ae)**

Compound was obtained via [typical procedure A] using vinylmagnesium bromide (390.0 μ L, 1.0 M (tetrahydrofuran), 0.390 mmol, 1.30 equiv.) and N,N-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**53aa**) (88.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 84% yield (80.4

mg, 0.252 mmol). mp: 101.3 – 101.9 °C; R_f : 0.30; Rs: >98:2; dr: >98:2; ^1H NMR (500 MHz, CDCl_3) δ 7.16 – 7.09 (m, 4H), 7.06 – 7.00 (m, 3H), 7.00 – 6.94 (m, 3H), 5.59 (ddd, J = 17.0, 10.1, 9.0 Hz, 1H), 5.43 (dd, J = 17.0, 1.5 Hz, 1H), 5.15 (dd, J = 10.2, 1.5 Hz, 1H), 3.63 – 3.50 (m, 2H), 3.37 (d, J = 6.5 Hz, 1H), 3.12 (dq, J = 13.9, 7.0 Hz, 1H), 3.03 (dd, J = 8.9, 6.5 Hz, 1H), 3.01 – 2.94 (m, 1H), 1.09 (t, J = 7.1 Hz, 3H), 0.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.7, 136.6, 136.2, 135.9 (+), 128.6 (+, 2C), 128.6 (+, 2C), 128.3 (+, 2C), 127.7 (+, 2C), 126.7 (+), 126.0 (+), 116.4 (-), 45.6, 41.3 (-), 39.7 (-), 36.3 (+), 31.5 (+), 12.5 (+), 12.4 (+); FTIR (KBr, cm^{-1}): 3059, 3027, 2976, 2934, 1630, 1445, 1428, 1276, 1134, 908, 753, 697; HRMS (TOF ES): Found 342.1820, calculated for $\text{C}_{22}\text{H}_{25}\text{NONa}$ ($\text{M}+\text{Na}$) 342.1834 (4.1 ppm).

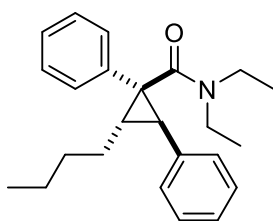


(1*R,2*S**,3*S**)-2-butyl-*N,N*-diethyl-1-phenyl-3-**

((trimethylsilyl)methyl)cyclopropane-1-carboxamide (94bc)

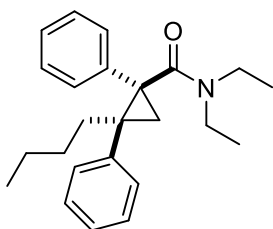
Compound was obtained via [typical procedure A] using (trimethylsilyl)methylmagnesium chloride (300 μL , 1.3 M (tetrahydrofuran), 0.390 mmol, 1.3 equiv.) and 2-butyl-*N,N*-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (82.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a pale yellow oil in 75% yield (80.7 mg, 0.224 mmol). R_f : 0.46; Rs: 75:25 (Vicinal Product Major); dr: >98:2; ^1H NMR (500 MHz, CDCl_3) δ 7.28 – 7.15 (m, 5H), 3.62 (dq, J = 14.4, 7.1 Hz, 1H), 3.49 (dq, J = 13.8, 7.0 Hz, 1H), 3.13 (dq, J = 13.9, 7.0 Hz, 1H), 2.94 (dq, J = 14.0, 7.0 Hz, 1H), 1.64 – 1.48 (m, 2H), 1.31 – 1.10 (m, 4H), 1.07 (t, J = 7.1 Hz, 3H), 1.05 – 0.97 (m, 1H), 0.87 – 0.76 (m, 2H), 0.69 (t, J = 7.0 Hz, 3H), 0.31 (t, J = 7.0 Hz, 3H), 0.17 (dd, J = 14.4, 11.9 Hz, 1H), 0.08 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.5, 138.8, 128.9 (+, 2C), 128.2 (+, 2C), 126.3 (+), 41.4 (-), 41.3, 39.6 (-), 31.6 (+), 31.0 (-), 28.7 (-), 23.6 (+), 22.6 (-), 16.3 (-), 14.0 (+), 12.6 (+), 12.3 (+), -1.2 (+, 3C); FTIR (KBr, cm^{-1}): 3057, 2955, 2932,

2872, 1633, 1457, 1423, 1271, 1247, 860, 838, 758, 701; HRMS (TOF ES): Found 382.2552, calculated for $C_{22}H_{37}NOSiNa$ ($M+Na$) 382.2542 (2.6 ppm).



(1*R,2*S**,3*R**)-2-butyl-N,N-diethyl-1,3-diphenylcyclopropane-1-carboxamide (94bd)**

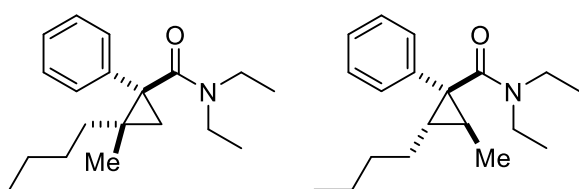
Compound was obtained via [typical procedure A] using phenylmagnesium bromide (130.0 μ L, 3.0 M (diethyl ether), 0.390 mmol, 1.30 equiv.) and 2-butyl-N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (82.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless oil in 91% yield (95.1 mg, 0.272 mmol). R_f : 0.40; Rs: 70:30 (Vicinal Product Major); dr: >98:2; 1H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.32 (m, 2H), 7.29 – 7.26 (m, 3H), 7.26 – 7.23 (m, 2H), 7.21 – 7.17 (m, 1H), 3.49 – 3.25 (m, 2H), 2.79 (d, J = 6.8 Hz, 1H), 2.73 (dq, J = 14.0, 7.1 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.40 (dq, J = 14.0, 7.0 Hz, 1H), 1.41 – 1.14 (m, 5H), 0.94 – 0.81 (m, 1H), 0.77 (t, J = 7.3 Hz, 3H), 0.65 (t, J = 7.1 Hz, 3H), 0.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 137.9, 137.9, 128.7 (+, 2C), 128.5 (+, 2C), 128.2 (+, 2C), 127.5 (+, 2C), 126.8 (+), 126.3 (+), 45.9, 40.8 (-), 39.1 (-), 33.6 (+), 31.0 (-), 30.2 (+), 28.7 (-), 22.5 (-), 14.1 (+), 11.9 (+), 11.7 (+); FTIR (KBr, cm^{-1}): 3058, 3023, 2957, 2932, 2870, 1631, 1445, 1379, 1274, 1080, 700; HRMS (TOF ES): Found 372.2321, calculated for $C_{24}H_{31}NONa$ ($M+Na$) 372.2303 (4.8 ppm).



(1*R,2*S**)-2-butyl-N,N-diethyl-1,2-diphenylcyclopropane-1-carboxamide (93bd)**

R_f : 0.26; dr: >98:2; 1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.21 (m,

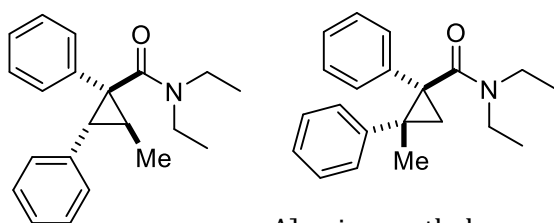
1H), 7.19 – 7.14 (m, 1H), 3.73 (dq, $J = 14.2, 7.1$ Hz, 1H), 3.11 – 2.90 (m, 2H), 2.79 (dq, $J = 13.8, 7.0$ Hz, 1H), 2.32 (d, $J = 5.3$ Hz, 1H), 2.30 – 2.21 (m, 1H), 1.30 (d, $J = 5.3$ Hz, 1H), 1.20 – 1.03 (m, 4H), 1.02 – 0.93 (m, 1H), 0.71 (t, $J = 7.0$ Hz, 3H), 0.65 (t, $J = 7.0$ Hz, 3H), 0.46 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.4, 140.1, 139.1, 130.4 (+, 2C), 128.9 (+, 2C), 128.4 (+, 2C), 127.8 (+, 2C), 126.8 (+), 126.2 (+), 42.9, 41.7 (-), 39.3 (-), 37.5, 36.8 (-), 29.4 (-), 22.8 (-), 22.6 (-), 14.2 (+), 13.4 (+), 11.8 (+).



(1S*,2S*)-2-butyl-N,N-diethyl-2-methyl-1-phenylcyclopropane-1-carboxamide (97b)

Compound was obtained via [typical procedure A] using methylmagnesium bromide (130.0 μL , 3.0 M (tetrahydrofuran), 0.390 mmol, 1.30 equiv.) and 2-butyl-N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (82.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless oil in 90% yield (77.3 mg, 0.269 mmol). R_f : 0.29; Rs: 88:12 (Geminal Product Major); dr: >98:2; ^1H NMR (500 MHz, CDCl_3) Mix of Regioisomers: δ [7.48 – 7.39 (m), $\Sigma 2\text{H}$], [7.30 – 7.23 (m), $\Sigma 2\text{H}$], [7.21 – 7.15 (m), $\Sigma 1\text{H}$], [3.68 – 3.49 (m) & 3.44 – 3.28 (m) & 3.18 (dq, $J = 14.0, 7.1$ Hz) & 3.07 (dq, $J = 13.9, 7.0$ Hz) & 2.96 (dq, $J = 14.0, 7.0$ Hz), $\Sigma 4\text{H}$], [1.62 – 1.54 (m) & 1.36 – 0.97 (m), $\Sigma 8\text{H}$], [1.29 (d, $J = 5.0$ Hz) & 1.22 (s), $\Sigma 3\text{H}$], [1.01 (t, $J = 7.1$ Hz), $\Sigma 3\text{H}$], [0.83 (t, $J = 7.1$ Hz) & 0.75 (t, $J = 7.1$ Hz), $\Sigma 3\text{H}$], [0.71 (t, $J = 7.4$ Hz) & 0.33 (t, $J = 7.0$ Hz), $\Sigma 3\text{H}$]; ^{13}C NMR (126 MHz, CDCl_3) Mix of Regioisomers: δ [171.0 & 170.8], [138.6 & 138.3], [129.4 (+) & 129.3 (+), $\Sigma 2\text{C}$], [128.1 (+) & 128.0 (+), $\Sigma 2\text{C}$], [126.4 (+) & 126.2 (+)], [41.4 (-) & 41.0 (-)], [40.8 & 39.8], [39.4 (-) & 39.1 (-)], [35.2 (-) & 31.2 (+) & 31.1 (-) & 28.5 (-) & 28.4 & 28.3 (-) & 24.0 (-) & 22.8 (-) & 22.3 (-) & 22.0 (+) & 21.9 (+) & 14.2 (+) & 14.0 (+) & 13.9 (+) & 13.5 (+) & 12.5 (+) & 12.4 (+) & 12.2 (+), $\Sigma 9\text{C}$]; FTIR (KBr, cm^{-1}): 3047, 2958,

2932, 2871, 1632, 1457, 1421, 1269, 1105, 729, 701; HRMS (TOF ES): Found 310.2143, calculated for $C_{19}H_{29}NONa$ ($M+Na$) 310.2147 (1.3 ppm).



(1*S,2*S**,3*R**)-N,N-diethyl-2-methyl-1,3-diphenylcyclopropane-1-carboxamide (98a)**

Compound was obtained via [typical procedure

A] using methylmagnesium bromide (130.0 μ L, 3.0 M (tetrahydrofuran),

0.390 mmol, 1.30 equiv.) and N,N-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**53aa**)

(88.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using

silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a

colorless amorphous solid in 92% yield (85.3 mg, 0.277 mmol). *R*_f: 0.26; *R*_s: 91:9 (Vicinal Product

Major); dr: >98:2 ¹H NMR (500 MHz, CDCl₃): Mix of regioisomers: δ [7.11 – 7.07 (m), Σ 4H], [7.03

– 6.98 (m), Σ 3H], [6.98 – 6.92 (m), Σ 3H], [3.70 (dq, *J* = 14.3, 7.1 Hz) & 3.58 (dq, *J* = 13.9, 7.1 Hz) &

3.41 – 3.34 (m) & 3.13 (dq, *J* = 13.5, 7.0 Hz) & 3.07 (dq, *J* = 14.2, 7.2 Hz), Σ 4H], [3.01 (d, *J* = 6.7 Hz)

& 2.08 (d, *J* = 5.4 Hz), Σ 1H], [2.40 (dt, *J* = 6.3 Hz) & 1.50 (d, *J* = 5.4 Hz), Σ 1H], [1.61 (s) & 1.31 (d, *J*

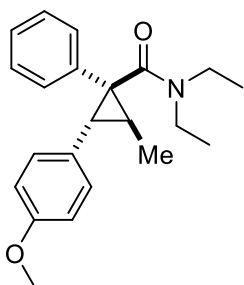
= 6.2 Hz), Σ 3H], [1.11 (t, *J* = 7.1 Hz), Σ 3H], [0.84 (t, *J* = 7.1 Hz) & 0.40 (t, *J* = 7.0 Hz, 1H), Σ 3H]; ¹³C

NMR (126 MHz, CDCl₃) δ 170.3, 137.6, 137.1, 128.9 (+, 2C), 128.6 (+, 2C), 128.1 (+, 2C), 127.6 (+,

2C), 126.4 (+), 125.7 (+), 44.7, 41.4 (-), 39.7 (-), 36.6 (+), 21.3 (+), 14.4 (+), 12.6 (+), 12.5 (+); FTIR

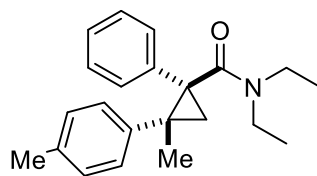
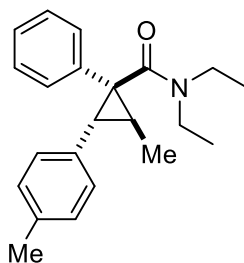
(KBr, cm⁻¹): 3041, 2967, 1629, 1458, 1425, 1276, 1140, 697; HRMS (TOF ES): Found 330.1840,

calculated for $C_{21}H_{25}NONa$ ($M+Na$) 330.1834 (1.8 ppm).



(1*S,2*R**,3*S**)-N,N-diethyl-2-(4-methoxyphenyl)-3-methyl-1-phenylcyclopropane-1-carboxamide (98c)**

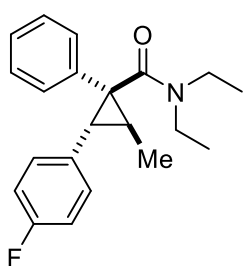
Compound was obtained via [typical procedure A] using methylmagnesium bromide (130 μ L, 3.0 M (tetrahydrofuran), 0.390 mmol, 1.30 equiv.) and N,N-diethyl-2-(4-methoxyphenyl)-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (96.5 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a mixture of regioisomers as a colorless oil in 52% yield (52.2 mg, 0.155 mmol). *R*_f: 0.23; Pdt ratio: 90:10; dr: >98:2; ¹H NMR (500 MHz, CDCl₃) δ 7.12 – 7.06 (m, 4H), 7.05 – 6.98 (m, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 2H), 3.73 – 3.66 (m, 1H), 3.65 (s, 3H), 3.58 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.13 (dq, *J* = 14.0, 7.0 Hz, 1H), 3.04 (dq, *J* = 14.0, 6.9 Hz, 1H), 2.94 (d, *J* = 6.6 Hz, 1H), 2.40 – 2.25 (m, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H), 0.40 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.4, 157.6, 137.3, 129.7, 129.5 (+, 2C), 128.8 (+, 2C), 128.2 (+, 2C), 126.3 (+), 113.1 (+, 2C), 55.2 (+), 44.4, 41.4 (-), 39.7 (-), 35.9 (+), 21.4 (+), 14.4 (+), 12.6 (+), 12.5 (+); FTIR (KBr, cm⁻¹): 3057, 2965, 2934, 2871, 1628, 1515, 1426, 1277, 1247, 1036, 821, 756, 700; HRMS (TOF ES): Found 360.1927, calculated for C₂₂H₂₇NO₂Na (M+Na) 360.1939 (3.3 ppm).



(1*S*,2*S*,3*R*)-N,N-diethyl-2-methyl-1-phenyl-3-(p-tolyl)cyclopropane-1-carboxamide (98d)

Compound was obtained via [typical procedure A] using methylmagnesium bromide (130 μ L, 3.0 M (tetrahydrofuran), 0.390 mmol, 1.30 equiv.) and N,N-diethyl-1-phenyl-2-(p-tolyl)cycloprop-2-ene-1-carboxamide (**53aa**) (92.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl

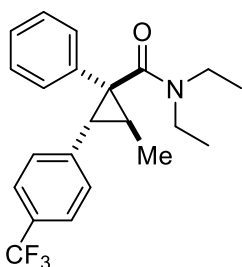
acetate mobile phase. The titled compound was obtained as a mixture of regioisomers as a colorless solid in 97 % yield (93.5 mg, 0.291 mmol). mp: 115.7 – 118.3 °C; R_f : 0.26; Pdt ratio: 86:14; dr: >98:2; ^1H NMR (500 MHz, CDCl_3): δ [7.13 – 7.07 (m, $\Sigma 4\text{H}$)], [7.05 – 6.99 (m, $\Sigma 1\text{H}$)], [6.87 – 6.79 (m, $\Sigma 4\text{H}$)], [3.70 (dq, $J = 14.3, 7.1$ Hz) & 3.58 (dq, $J = 14.0, 7.1$ Hz) & 3.42 – 3.33 (m) & 3.12 (dq, $J = 14.0, 7.0$ Hz) & 3.05 (dq, $J = 14.0, 7.0$ Hz), $\Sigma 4\text{H}$], [2.96 (d, $J = 6.7$ Hz) & 2.39 – 2.32 (m) & 2.02 (d, $J = 5.7$ Hz), $\Sigma 2\text{H}$], [2.21 (s) & 2.14 (s), $\Sigma 3\text{H}$], [1.58 (s) & 1.30 (d, $J = 6.2$ Hz), $\Sigma 3\text{H}$], [1.11 (t, $J = 7.1$ Hz), $\Sigma 3\text{H}$], [0.82 (t, $J = 7.0$ Hz) & 0.40 (t, $J = 7.0$ Hz), $\Sigma 3\text{H}$]; ^{13}C NMR (126 MHz, CDCl_3) δ [170.6 & 170.3, $\Sigma 1\text{C}$], [139.2 & 138.1 & 137.2 & 135.5 & 135.0 & 134.4, $\Sigma 3\text{C}$], [128.9 (+) & 128.7 (+) & 128.6 (+) & 128.4 (+) & 128.4 (+) & 128.3 (+) & 128.1 (+) & 127.8 (+), $\Sigma 8\text{C}$], [126.3 (+) & 126.0 (+), $\Sigma 1\text{C}$], [57.1 & 44.6, $\Sigma 1\text{C}$], [41.6 (-) & 41.3 (-) & 39.7 (-) & 39.3 (-), $\Sigma 2\text{C}$], [36.3 (+) & 26.8, $\Sigma 1\text{C}$], [24.1 (-) & 21.4 (+), $\Sigma 1\text{C}$], [21.1 (+) & 21.0 (+), $\Sigma 1\text{C}$], [14.5 (+) & 14.4 (+), $\Sigma 1\text{C}$], [12.5 (+) & 12.5 (+) & 12.5 (+), $\Sigma 2\text{C}$]; FTIR (KBr, cm^{-1}): 3062, 2968, 2932, 2871, 1632, 1457, 1425, 1276, 1219, 1140, 811, 700; HRMS (TOF ES): Found 344.1989, calculated for $\text{C}_{22}\text{H}_{27}\text{NONa}$ ($\text{M}+\text{Na}$) 344.1990 (0.3 ppm).



(1S,2R,3S)-N,N-diethyl-2-(4-fluorophenyl)-3-methyl-1-phenylcyclopropane-1-carboxamide (98e)

Compound was obtained via [typical procedure A] using methylmagnesium bromide (130 μL , 3.0 M (tetrahydrofuran), 0.390 mmol, 1.30 equiv.) and N,N-diethyl-2-(4-fluorophenyl)-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (93.0 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a mixture of regioisomers as a colorless oil in 99% yield (97.0 mg, 0.298 mmol). R_f : 0.16; Pdt Ratio: 95:5; dr:

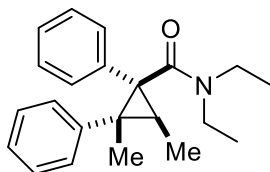
>98:2; ^1H NMR (500 MHz, CDCl_3) mixture of regioisomers: δ [7.13 – 7.04 (m), $\Sigma 4\text{H}$], [7.04 – 6.99 (m), $\Sigma 1\text{H}$], [6.92 – 6.86 (m), $\Sigma 2\text{H}$], [6.79 – 6.73 (m) & 6.71 – 6.65 (m), $\Sigma 2\text{H}$], [3.67 (dq, J = 14.4, 7.1 Hz) & 3.58 (dq, J = 13.8, 7.1 Hz) & 3.12 (dq, J = 13.9, 7.0 Hz) & 3.04 (dq, J = 14.0, 7.0 Hz), $\Sigma 4\text{H}$], [2.97 (d, J = 6.6 Hz) & 2.38 – 2.31 (m) & 2.07 (d, J = 5.5 Hz) & 1.45 (d, J = 5.3 Hz), $\Sigma 2\text{H}$], [1.58 (s) & 1.30 (d, J = 6.2 Hz), $\Sigma 3\text{H}$], [1.11 (t, J = 7.1 Hz), $\Sigma 3\text{H}$], [0.84 (t, J = 7.1 Hz) & 0.39 (t, J = 7.0 Hz), $\Sigma 3\text{H}$]; ^{13}C NMR (126 MHz, CDCl_3) major regioisomer: δ 170.1, 161.1 (d, J = 243.9 Hz), 136.9, 133.3 (d, J = 2.8 Hz), 129.9 (+, d, J = 8.1 Hz, 2C), 128.7 (+), 128.2 (+, 2C), 126.5 (+, 2C), 114.4 (+, d, J = 21.5 Hz, 2C), 44.5, 41.4 (-), 39.7 (-), 35.8 (+), 21.4 (+), 14.3 (+), 12.5 (+), 12.5 (+); ^{19}F NMR (376 MHz, CDCl_3) δ -117.6 (s, 1F); FTIR (KBr, cm^{-1}): 2969, 2934, 2872, 1629, 1512, 1426, 1216, 822, 761, 700; HRMS (TOF ES): Found 348.1744, calculated for $\text{C}_{21}\text{H}_{24}\text{FNO}_2\text{Na}$ ($\text{M}+\text{Na}$) 348.1740 (1.1 ppm).



(1*S,2*S**,3*R**)-N,N-diethyl-2-methyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)cyclopropane-1-carboxamide (98f)**

Compound was obtained via [typical procedure A] using methylmagnesium bromide (130 μL , 3.0 M (tetrahydrofuran), 0.390 mmol, 1.30 equiv.) and N,N-diethyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)cycloprop-2-ene-1-carboxamide (**53aa**) (108 mg, 0.30 mmol, 1.0 equiv.). The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 93% yield (104.3 mg, 0.278 mmol). mp: 93.9 – 94.8 $^{\circ}\text{C}$; R_f : 0.29; Pdt ratio: >98:2; dr: >98:2; ^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, J = 8.3 Hz, 2H), 7.14 – 7.06 (m, 4H), 7.06 – 7.01 (m, 1H), 7.02 (d, J = 8.3 Hz, 2H), 3.68 (dq, J = 14.3, 7.1 Hz, 1H), 3.58 (dq, J = 14.1, 7.1 Hz, 1H), 3.17 – 3.01 (m, 2H), 3.05 (d, J = 6.6 Hz, 1H), 2.47 – 2.38 (m, 1H), 1.32 (d, J = 6.2 Hz, 3H), 1.11 (t, J = 7.0 Hz, 3H), 0.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.6, 141.9, 136.3, 128.7 (+), 128.5 (+, 2C), 128.3 (+, 2C), 127.7 (q, J = 32.0 Hz), 126.7 (+, 2C), 124.4 (q, J = 3.7

Hz, +, 2C), 124.3 (q, $J = 271.7$ Hz), 45.3, 41.3 (-), 39.7 (-), 36.1 (+), 21.7 (+), 14.1 (+), 12.4 (+), 12.4 (+); ^{19}F NMR (376 MHz, CDCl_3) δ -62.34 (s, 3F); FTIR (KBr, cm^{-1}): 2972, 2936, 1630, 1326, 1164, 1121, 1068, 1017, 860, 728, 701; HRMS (TOF ES): Found 398.1719, calculated for $\text{C}_{22}\text{H}_{24}\text{F}_3\text{NONa}$ ($\text{M}+\text{Na}$) 398.1708 (2.8 ppm).

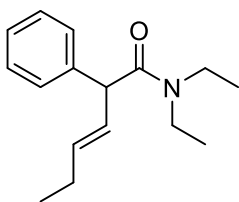


(1R,2R,3S)-N,N-diethyl-2,3-dimethyl-1,2-diphenylcyclopropane-1-carboxamide (99)

Methylmagnesium bromide (130 μL , 3.0 M (diethyl ether), 0.390 mmol, 1.35 equiv.) was added dropwise to a flame dried two neck flask containing copper iodide (3.0 mg, 15.0 μmol , 5.0 mol%) and freshly dried and distilled tetrahydrofuran (4 mL) under a nitrogen atmosphere at 0 $^{\circ}\text{C}$. The mixture was stirred for five minutes at 0 $^{\circ}\text{C}$. N,N-diethyl-1,2-diphenylcycloprop-2-ene-1-carboxamide (**53aa**) (88.0 mg, 0.30 mmol, 1.0 equiv.) was then added slowly dropwise as a solution in dry tetrahydrofuran (2 mL). After 20 minutes of stirring at 0 $^{\circ}\text{C}$, iodomethane (28 μL , 64.0 mg, 0.45 mmol, 1.50 equiv.) was added dropwise and stirred for 30 minutes at 0 $^{\circ}\text{C}$. The reaction was then allowed to warm to room temperature over 15 minutes before saturated aqueous ammonium chloride (1 mL) was added. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography using silica and a 3:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a colorless solid in 91 % yield (87.5 mg, 0.272 mmol). mp: 150.3 – 151.2 $^{\circ}\text{C}$; R_f : 0.26; dr: >98:2; ^1H NMR (500 MHz, CDCl_3) δ 7.08 – 6.97 (m, 8H), 6.96 – 6.90 (m, 2H), 3.67 – 3.51 (m, 2H), 3.21 – 3.03 (m, 2H), 2.39 (q, $J = 6.5$ Hz, 1H), 1.61 (s, 3H), 1.36 (d, $J = 6.5$ Hz, 3H), 1.12 (t, $J = 7.1$ Hz, 3H), 0.44 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.5, 144.9, 138.7, 129.4 (+, 2C), 127.9 (+, 2C), 127.8 (+), 127.7 (+, 2C), 125.9 (+, 2C), 125.5 (+), 42.4, 41.6 (-), 38.7 (-), 38.2,

23.5 (+), 21.5 (+), 12.7 (+), 12.7 (+), 10.5 (+); FTIR (KBr, cm^{-1}): 3059, 2969, 1624, 1444, 1422, 1267, 1066, 694; HRMS (TOF ES): Found 344.1996, calculated for $\text{C}_{22}\text{H}_{27}\text{NONa}$ ($\text{M}+\text{Na}$) 344.1990 (1.7 ppm).

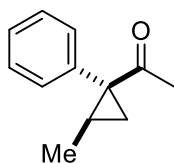
3.13.5 Miscellaneous



(E)-N,N-diethyl-2-phenylhex-3-enamide (72g)

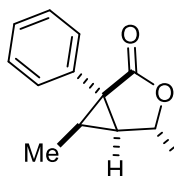
Ethylmagnesium bromide (135 μL , 3.0 M (diethyl ether), 0.405 mmol, 1.35 equiv.) was added dropwise to a flame dried two neck flask containing copper iodide (3.0 mg, 15.0 μmol , 5.0 mol%) and freshly dried and distilled dimethoxyethane (1.0 mL) under a nitrogen atmosphere at 0 $^{\circ}\text{C}$. The mixture was stirred for five minutes at 0 $^{\circ}\text{C}$. N,N-diethyl-1-phenylcycloprop-2-ene-1-carboxamide (**53aa**) (65.0 mg, 0.30 mmol, 1.0 equiv.) was then added slowly dropwise as a solution in dry dimethoxyethane (1.0 mL). The reaction was then stirred for 60 minutes at room temperature. Saturated aqueous ammonium chloride (1 mL) was added slowly dropwise. The resulting solution was then diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were washed with brine, dried, filtered, and evaporated. The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 77% yield (56.4 mg, 0.230 mmol). R_f : 0.26; ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.19 (m, 5H), 5.87 (dd, J = 15.4, 8.0 Hz, 1H), 5.51 (dt, J = 15.4, 6.3 Hz, 1H), 4.38 (d, J = 8.0 Hz, 1H), 3.55 – 3.44 (m, 1H), 3.38 – 3.14 (m, 3H), 2.11 – 1.99 (m, 2H), 1.11 (t, J = 7.1 Hz, 6H), 1.07 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.7, 140.2, 133.6 (+), 129.0 (+), 128.8 (+, 2C), 128.0 (+, 2C), 126.9 (+), 52.5 (+), 41.9 (-), 40.4 (-), 25.6 (-), 14.6 (+), 13.6 (+), 13.0 (+); FTIR (KBr, cm^{-1}): 3059, 3026, 2966, 2931, 2872, 1639, 1600, 1492, 1479, 1454,

1427, 1379, 1361, 1311, 1276, 1253, 1219, 1138, 1095, 1072, 966, 783, 752; HRMS (TOF ES): Found 246.1852, calculated for C₁₆H₂₄NO (M+H) 246.1858 (2.4 ppm).



1-((1*S,2*R**)-2-methyl-1-phenylcyclopropyl)ethan-1-one (74)**

Methylmagnesium bromide (130 μ L, 3.0 M (diethyl ether), 0.40 mmol, 2.0 equiv.) was added dropwise to (1*S**,2*R**)-*N*-methoxy-*N*,2-dimethyl-1-phenylcyclopropane-1-carboxamide (**53au**) (44.0 mg, 0.20 mmol, 1.0 equiv.) dissolved in dry dimethoxyethane in a flame dried two neck flask under a nitrogen atmosphere. The reaction was then stirred at 40 °C for 18 hours. After cooling to room temperature, saturated aqueous ammonium chloride (1 mL) was added dropwise. The resulting solution was diluted with water and extracted with diethyl ether (3 x 5 mL). Combined organic layers were dried, filtered, and evaporated. The product was purified by column chromatography using silica and a 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as a viscous colorless oil in 61% yield (21.2 mg, 0.122 mmol). *R*_f: 0.32; ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.16 (m, 5H), 1.90 (s, 3H), 1.70 (ddq, *J* = 8.7, 7.2, 6.2 Hz, 1H), 1.58 (dd, *J* = 7.1, 4.0 Hz, 1H), 1.12 (d, *J* = 6.2 Hz, 3H), 1.01 (dd, *J* = 8.7, 4.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 206.9, 142.6, 130.5 (+, 2C), 128.8 (+, 2C), 127.4 (+), 43.3, 30.8 (+), 25.5 (+), 22.0 (-), 12.3 (+); FTIR (KBr, cm⁻¹): 3022, 3001, 2955, 2928, 2874, 1691, 1600, 1492, 1456, 1444, 1435, 1361, 1280, 1165, 1132, 1097, 1074, 1024, 979, 758; HRMS (TOF ES): Found 192.1386, calculated for C₁₂H₁₈NO (M+NH₄) 192.1388 (1.0 ppm).



(1*R,4*S**,5*S**,6*R**)-4-(tert-butyl)-6-methyl-1-phenyl-3-**

oxabicyclo[3.1.0]hexan-2-one (85)

p-Toluenesulfonic acid monohydrate (47.0 mg, 0.25 mmol, 1.2 equiv.) was added to (1*R**,2*R**,3*S**)-2-((*R**)-1-hydroxy-2,2-dimethylpropyl)-*N*-methoxy-*N*,3-dimethyl-1-

phenylcyclopropane-1-carboxamide (**53au**) (61.0 mg, 0.20 mmol, 1.0 equiv.) dissolved in benzene (5 mL) and stirred for 10 minutes. The reaction was then warmed to 50 °C and stirred for one hour. After cooling to room temperature, potassium carbonate (35 mg, 0.25 mmol, 1.2 equiv.) was added and stirred for 15 minutes. The reaction was then filtered through a silica plug using ethyl acetate, evaporated, and further purified by silica gel column chromatography using 6:1 hexane:ethyl acetate mobile phase. The titled compound was obtained as colorless oil in 89% yield (43.4 mg, 0.177 mmol). *R*_f: 0.37; ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.32 (m, 2H), 7.30 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 3.86 (s, 1H), 2.32 (d, *J* = 8.2 Hz, 1H), 1.76 (dq, *J* = 8.2, 6.5 Hz, 1H), 1.21 (d, *J* = 6.5 Hz, 3H), 0.98 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 174.5, 135.5, 128.7 (+, 2C), 127.8 (+, 2C), 127.5 (+), 83.4 (+), 37.5, 34.6, 31.5 (+), 25.2 (+, 3C), 25.0 (+), 8.4 (+); FTIR (KBr, cm⁻¹): 3060, 2962, 2907, 2873, 1759, 1500, 1335, 1112, 994, 908, 754, 697; HRMS (TOF ES): Found 267.1358, calculated for C₁₆H₂₀O₂Na (M+Na) 267.1361 (1.1 ppm).

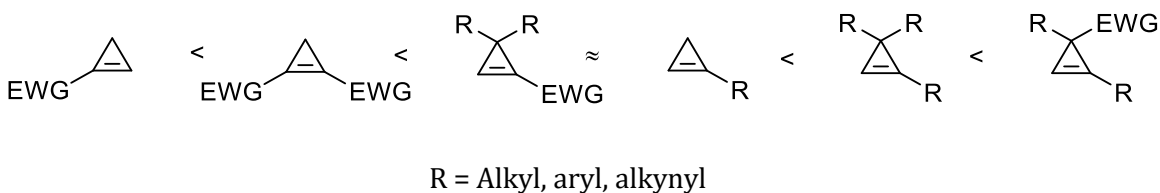
Chapter 4. Review of Nucleophilic Additions to Cyclopropenes

4.1 Introduction

The expansive chemistry of the smallest cyclic olefin, cyclopropene, has been detailed in several recent reviews.^[54-61] These reviews have detailed the use of cyclopropenes' large amount of strain energy (approximately 55 kcal/mol) to facilitate a variety of Lewis acid promoted, radical, and organometallic reactions. However, the use of cyclopropene as the electrophilic component of a variety of newly developed nucleophilic addition reactions has not been comprehensively compiled. Thus, this review will highlight nucleophilic addition reactions to cyclopropenes published since 2005 and will only focus on reactions involving a non-concerted addition mechanism.

The stability of cyclopropenes varies dramatically depending on both the location of and identity of substituents located on the 3-membered ring (**Figure 8**). Cyclopropenes possessing electron-withdrawing substituents at C-1 or C-2 are considered highly unstable due to their high reactivity as Michael acceptors. Replacement of the hydrogens at C-3 provides significant stabilization by eliminating the possibility of the ene-reaction. Large substituents at C-1 or C-2 provide stabilization via steric shielding of the strained double bond. A combination of stabilizing substituents at multiple locations of the ring can result in cyclopropenes which are shelf stable from several days to many months.

Figure 8. Stability of various cyclopropenes

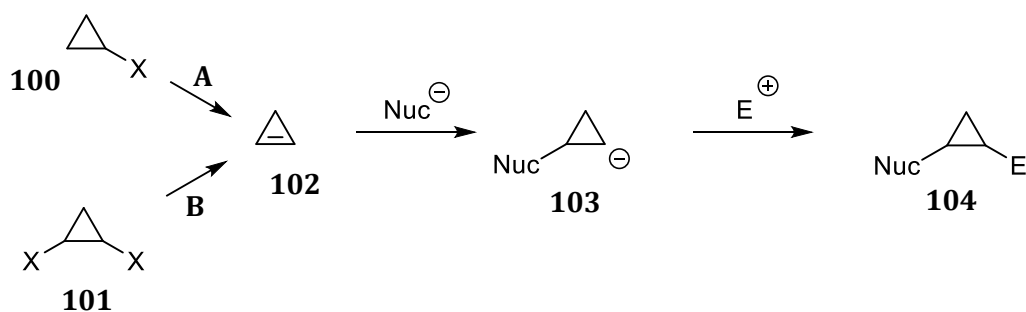


4.2 Nucleophilic Additions to *In-Situ* Generated Cyclopropenes

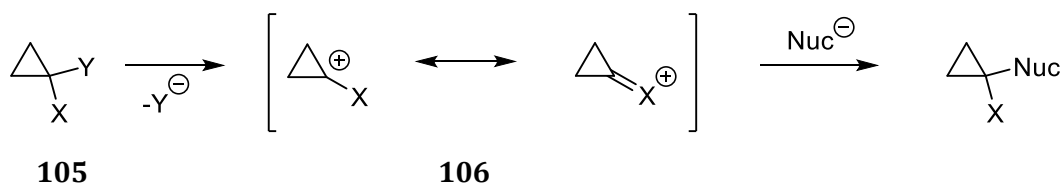
Two of the most common methods for the generation of cyclopropenes involve a base-assisted 1,2-dehydrohalogenation of cyclopropyl halides **100** (**Scheme 41a, Path A**)^[62, 63] and the 1,2-dehalogenation of dihalogenated cyclopropanes **101** using organolithium reagents (**Scheme 41a, Path B**).^[64] Following the elimination event, the highly unstable cyclopropene intermediate **102** can be intercepted by a nucleophile prior to decomposition to provide cyclopropyl anion **103**. Exposure of this species to a suitable electrophile allows for the production of products **104**. This type of mechanism involving a stepwise elimination/addition sequence can be considered an overall formal nucleophilic substitution performed on cyclopropyl halides. This type of mechanism is in sharp contrast to cyclopropanes of type **105** in which similar formal substitution products are obtained via an E1-mechanism involving a stabilized carbocation intermediate **106**, which will not be detailed in this review (**Scheme 41b**).

Scheme 41.

a)



b)

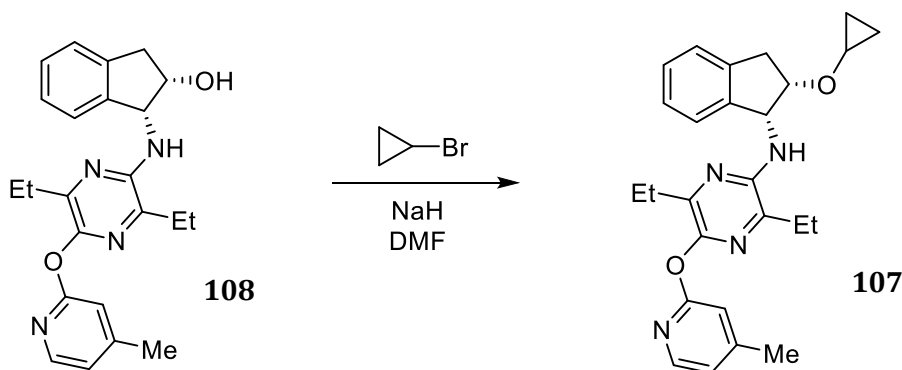


4.2.1 Nucleophilic Additions of Oxygen Nucleophiles

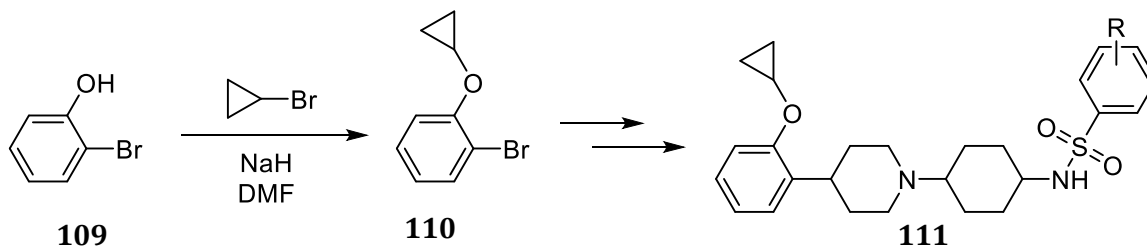
Cyclopropyl ethers can be obtained by exposure of cyclopropyl bromide to alcohols or phenols in the presence of a suitable base. This strategy found application during the synthesis of CRF₁ receptor antagonist **107** in which alcohol **108** underwent nucleophilic addition to cyclopropyl bromide in the presence of sodium hydride in DMF (**Scheme 42a**).^[65] Additionally, phenol **109** was shown to be a suitable nucleophile in the reaction with cyclopropyl bromide to provide cyclopropyl ether **110** which was then converted to adrenergic receptor antagonist **111** (**Scheme 42b**).^[66] Furthermore, the addition of phenoxide nucleophiles to cyclopropenes was used during the synthesis of antitumor and angioinhibitor **112** (**Scheme 43a**),^[67] plasmodium CDPK₄ inhibitor **113** (**Scheme 43b**),^[68] and kynurenine monooxygenase inhibitor **114** (**Scheme 44**).^[69]

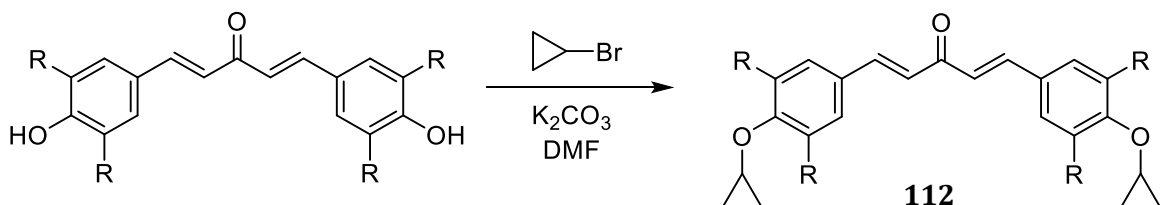
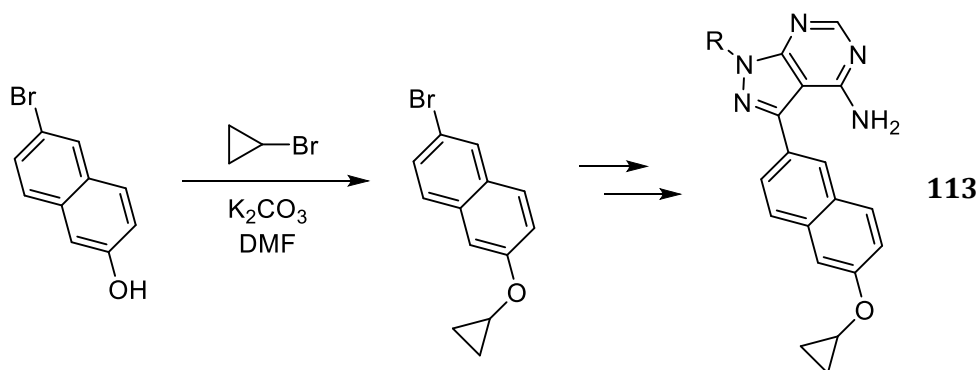
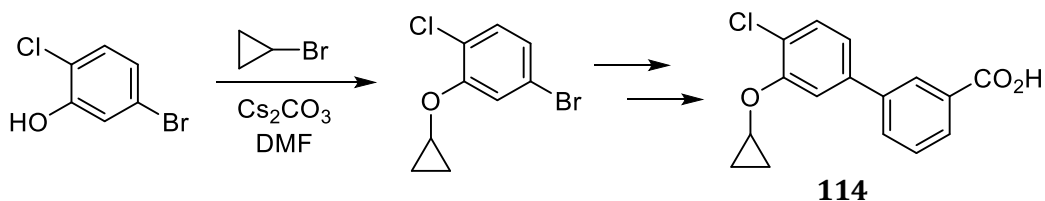
Scheme 42

a)



b)



Scheme 43.**a)****b)****Scheme 44.**

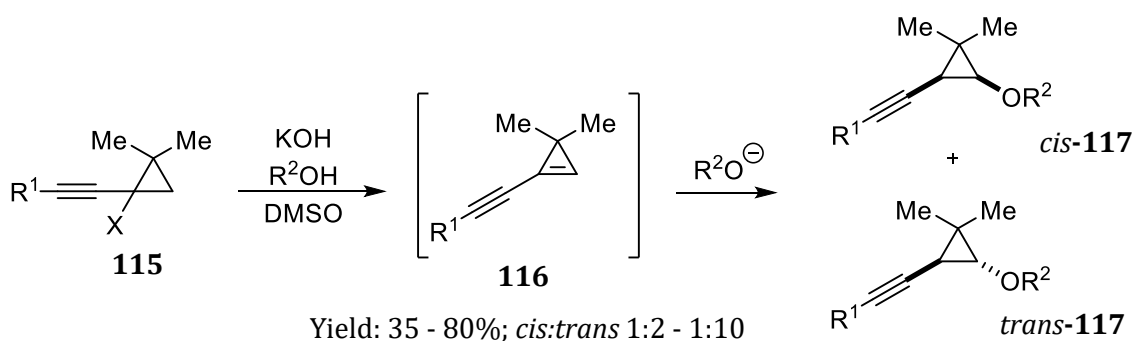
Even though cyclopropene intermediates were not identified during these transformations, it can be postulated that an elimination/addition sequence is the operating mechanism due to the difficulty of performing direct nucleophilic displacement on cyclopropane due to the unique near sp^2 hybridization of the carbon – bromine bond. The symmetric nature of the proposed cyclopropene intermediates in schemes 2, 3, and 4, negates a discussion of stereoselectivity.

Shavrin reported the first attempts to conduct stereoselective nucleophilic additions to cyclopropenes. In this report, cyclopropanes **115** underwent dehydrohalogenation to provide

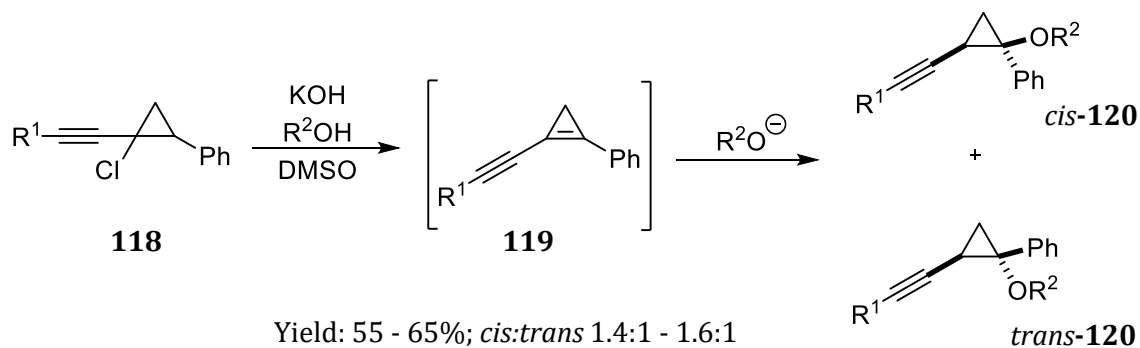
achiral cyclopropene **116**, which then underwent nucleophilic addition of various alkoxides to provide mixtures of products **117** with rather poor diastereoselectivity (**Scheme 45a**).^[70] Similarly, alkynylcyclopropane **118** proceeding via achiral cyclopropene intermediate **119** failed to produce meaningful diastereoselectivity by producing cyclopropane **120** as a mixture of diastereomers (**Scheme 45b**).^[70] Rather poor diastereoselectivity was also observed in the addition of ethoxide to highly strained cyclopropene **121** to provide products **122** (**Scheme 46**).^[70]

Scheme 45

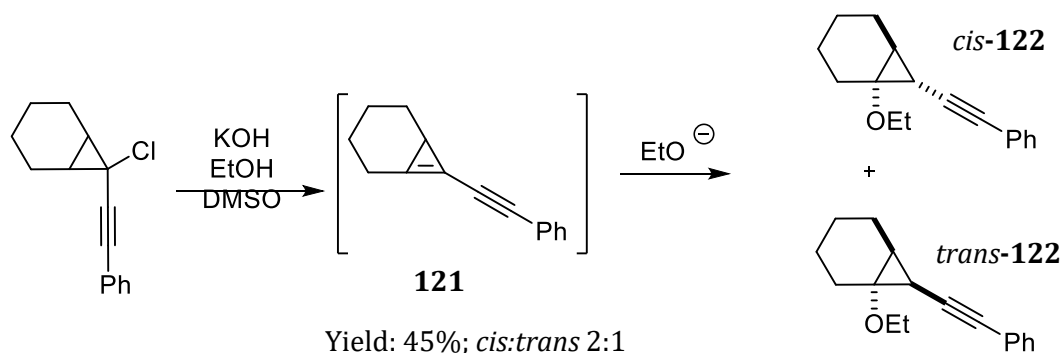
a)



b)



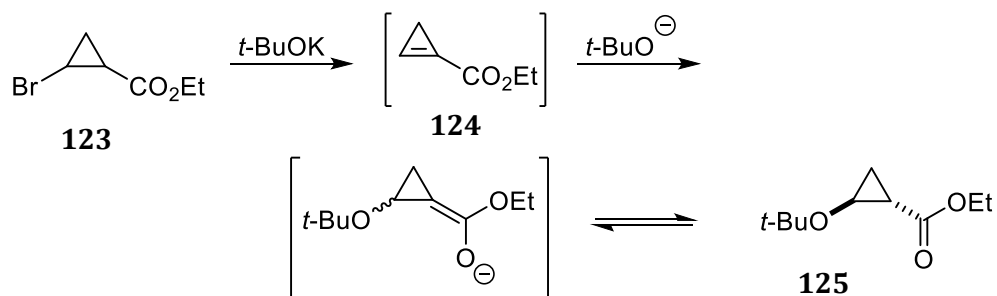
Scheme 46.



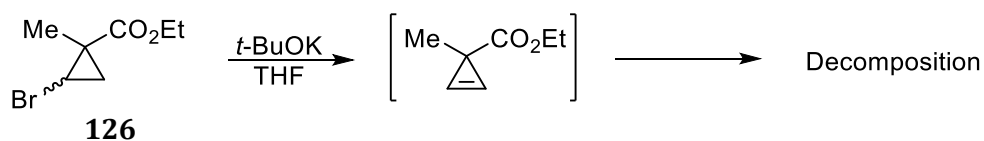
Wiberg first reported a highly diastereoselective nucleophilic addition to cyclopropenes using bromocyclopropane **123** in 1957.^[71] Exposure of **123** to potassium *tert*-butoxide produced cyclopropene intermediate **124** which then underwent conjugate addition of *tert*-butanol across the double bond. The incorporation of an ester function allowed for efficient epimerization of the alpha-center to selectively form the thermodynamically favored *trans*-configured product **125** (Scheme 47a).

Scheme 47

a)



b)

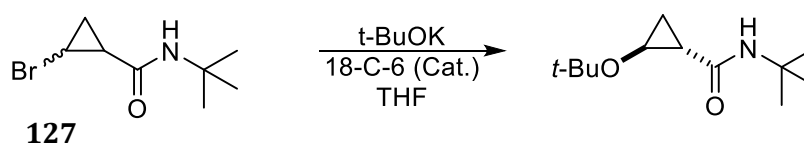


Much more recently, Rubin showed that this reaction only proceeds using very weak *t*-butoxide nucleophiles with substrates which form highly electrophilic conjugated cyclopropenes. Attempts to achieve the transformation with non-conjugated ester **126** only led to decomposition (**Scheme 47b**).^[72] Attempts to increase reactivity by using more nucleophilic secondary or primary nucleophiles in the reaction with **123** also only resulted in decomposition.

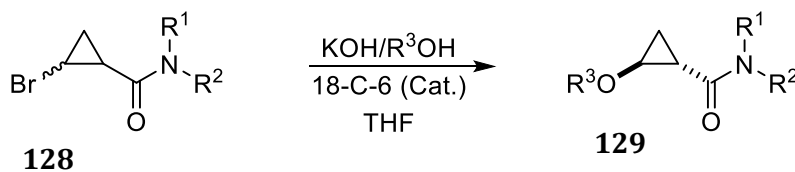
Replacement of the ester function with a less electrophilic carboxamide in substrate **127** allowed for the development of a general diastereoselective formal nucleophilic substitution of bromocyclopropanes with oxygen based nucleophiles under thermodynamic control (**Scheme 48a**). The use of potassium hydroxide instead of potassium *tert*-butoxide with carboxamides **128** allowed for the incorporation of phenoxides along with secondary and primary alkoxide nucleophiles into cyclopropanes **129** (**Scheme 48b**).^[73,74] It was reported that the addition of less nucleophilic alcohols and most phenols in the presence of KOH resulted in deteriorated diastereoselectivities which, was attributed to the reduced propensity of product to undergo epimerization. As a solution to this problem, recovered crude material could be subjected to *t*-BuOK in the presence of 18-C-6 to drastically increase the diastereomeric ratios (**Scheme 48b**).

Scheme 48

a)



b)

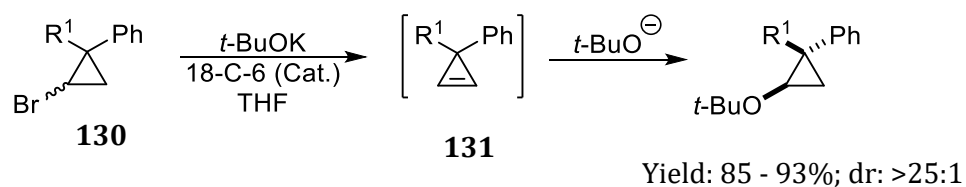


Yield: 44 - 93%; dr: 6:1 - 25:1

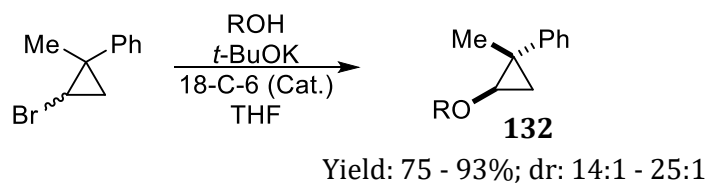
A second mode of diastereoselectivity was also demonstrated using bromocyclopropanes **130** which, after 1,2-dehydrobromination provides 3,3-disubstituted non-conjugated cyclopropene **131**. Subsequent nucleophilic addition of *tert*-butoxide occurs with facial selectivity as determined by the differing steric signature of the substituents in the 3-position (**Scheme 49a**).^[72,73] Additionally primary and secondary alkoxides were shown to outcompete *tert*-butoxide as the nucleophile and add selectively to cyclopropene to generate cyclopropyl ethers **132** (**Scheme 49b**).^[72,73] Utilization of cyclopropylcarboxamide **133** resulted in another mode of diastereoselectivity. In this system, the alkoxide nucleophile was delivered via efficient coordination with the amide function to provide *cis*-configured ethers **134** (**Scheme 49c**).^[72,73]

Scheme 49

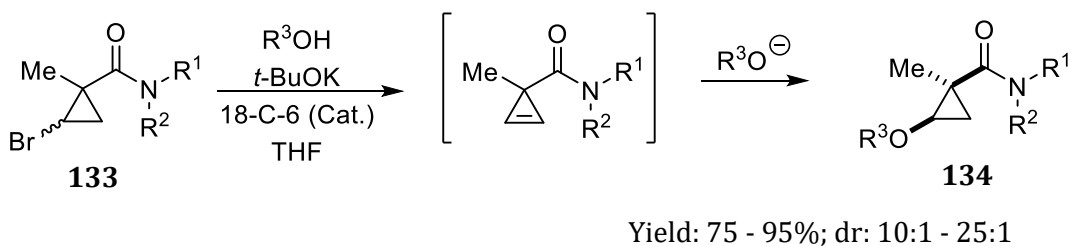
a)



b)

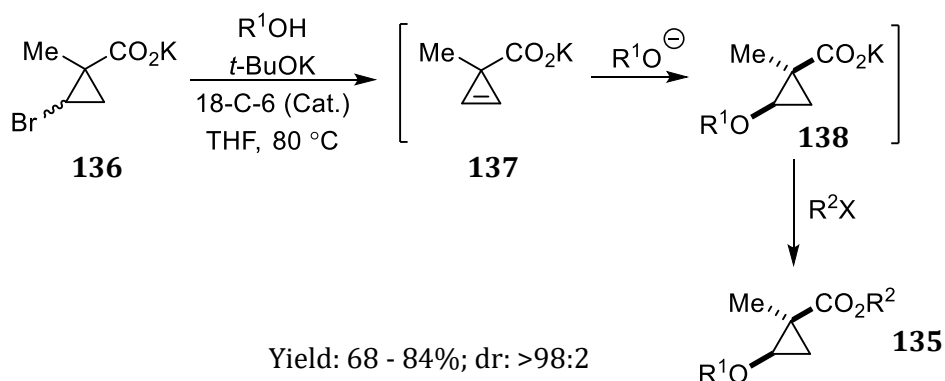


c)



Interestingly, *cis*-configured cyclopropylesters **135** could be accessed via use of carboxylate salts **136** (**Scheme 50**).^[72] 1,2-dehydrobromination of salts **136** provided cyclopropene intermediate **137** which then underwent carboxylate directed addition of various alkoxides to provide alkoxy cyclopropane salt **138**. Subsequent exposure of this species to S_N2-active electrophiles resulted in efficient alkylation of the carboxylate and cyclopropylesters **135**.

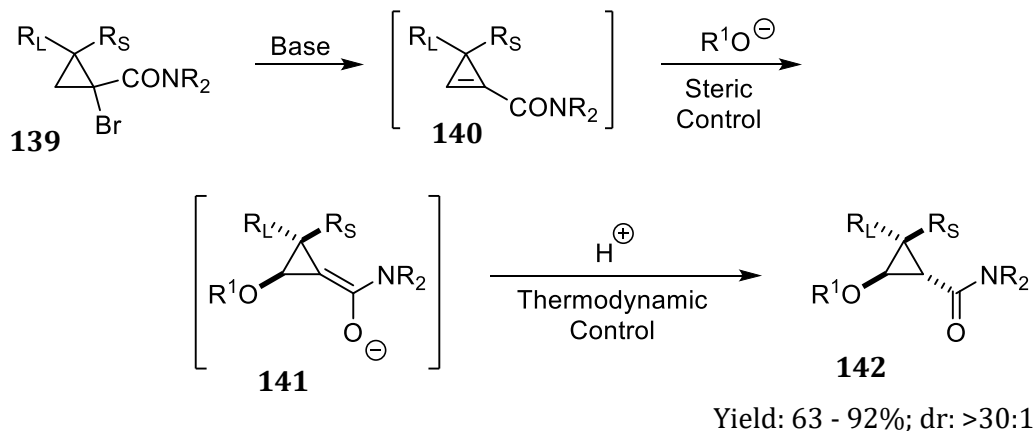
Scheme 50.



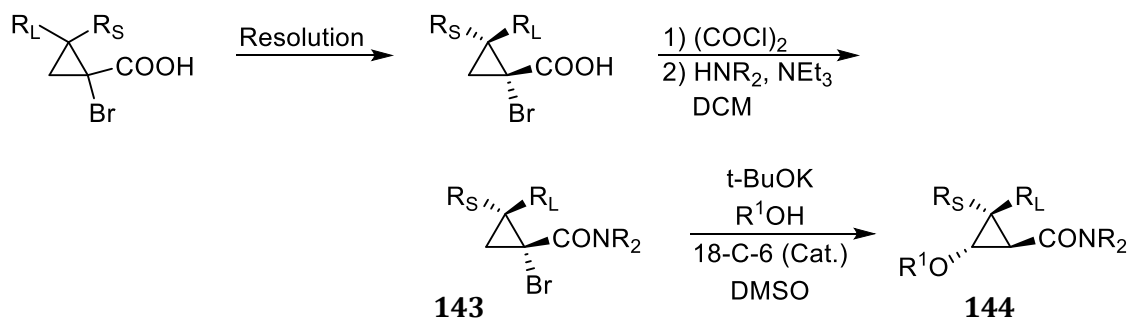
Both steric and thermodynamic modes of stereocontrol were combined during the formal nucleophilic substitution of cyclopropyl bromide **139** (**Scheme 51a**).^[75] In this process, 1,2-dehydrobromination occurs to provide tri-substituted conjugated cyclopropene intermediate **140**. Next, conjugate nucleophilic addition occurs with facial differentiation being determined by the steric signature of the substituents at C-3 to provide cyclopropyl enolate **141**. This species can then undergo efficient epimerization of the amide alpha-carbon to establish the thermodynamically favored product **142**. The ability to access optically active cyclopropyl bromides^[76] **143** via recrystallization of the corresponding carboxylic acid with cinchon alkaloids allows for synthesis of homochiral tetrasubstituted cyclopropanes **144** (**Scheme 51b**).^[75]

Scheme 51

a)



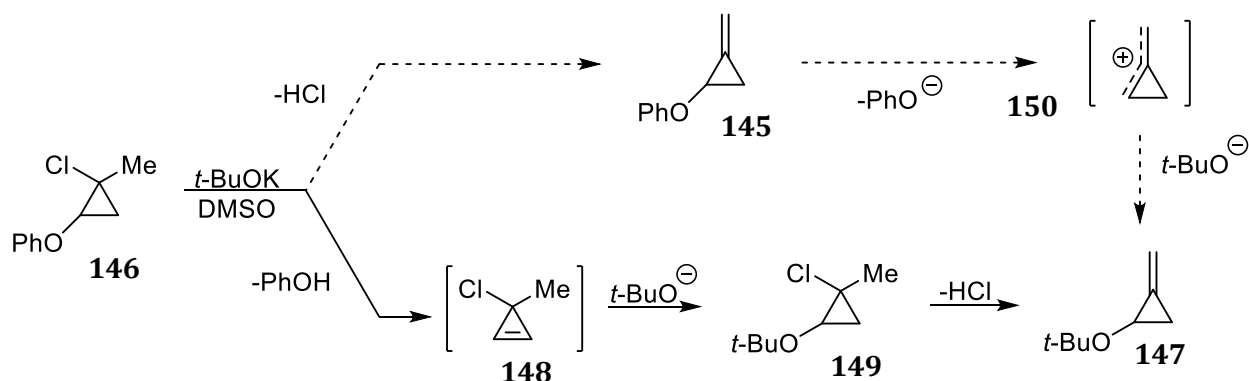
b)



In the attempted synthesis of methylenecyclopropane **145**, Zefirov proposed the elimination of phenol from chlorocyclopropane **146** as the first step leading to the observed product **147** (**Scheme 52**).^[77] Following the elimination of phenol, the resulting chlorocyclopropene **148** could then undergo nucleophilic addition of *tert*-butoxide to furnish cyclopropyl ether **149**. The subsequent elimination of HCl would then provide the observed product **147**. The formal nucleophilic substitution mechanism proposed by Zefirov is debatable due to an alternative plausible mechanism which would avoid the formation of a cyclopropene intermediate. Initial elimination of HCl along the exocyclic C- C bond would establish methylene cyclopropane **145**

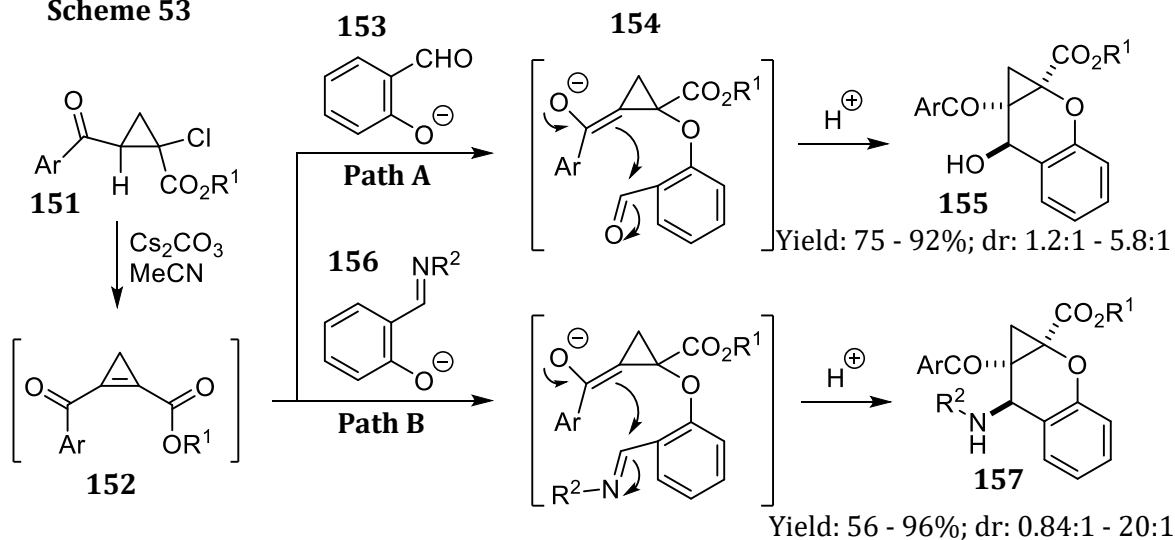
which could then undergo an S_N1 reaction via the formation of the stabilized allylic cationic intermediate **150** to also provide observed product **147**.

Scheme 52.



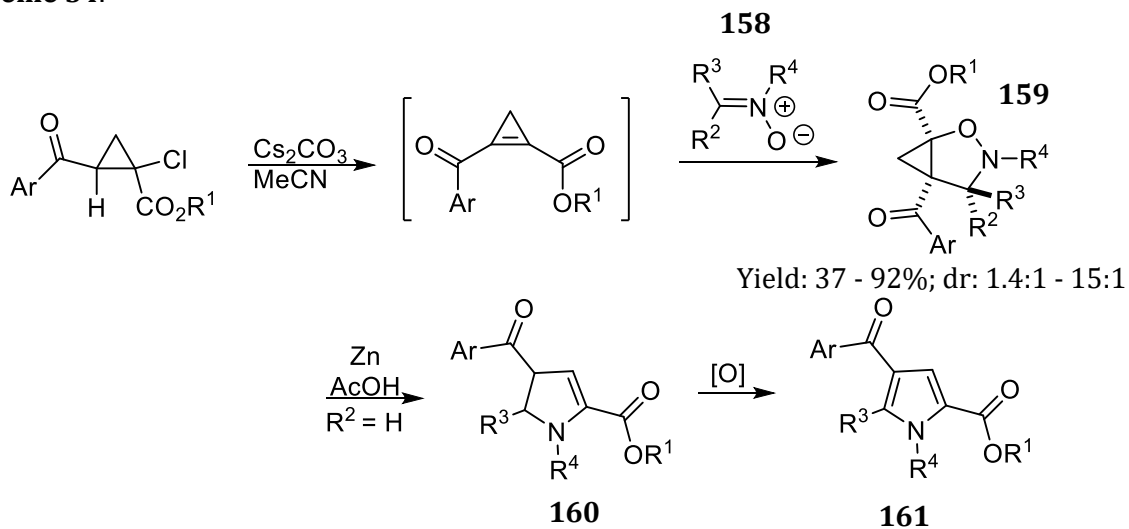
Gong has recently reported the addition of phenoxide nucleophiles to cyclopropenes followed by intramolecular quenching with carbon electrophiles (**Scheme 53**).^[78] Highly reactive β -keto-ester **151** was found to undergo highly efficient 1,2-dehydrochlorination to provide conjugated cyclopropene **152** in the presence of cesium carbonate. This species then underwent nucleophilic addition of the conjugate base of salicylic aldehyde **153** to provide cyclopropyl enolate **154**. A subsequent intramolecular aldol reaction resulted in tetrahydrocyclopropa[*b*]chromenes **155** in good yield with moderate diastereoselectivity (**Scheme 53, Path A**). Additionally, the use of salicylic imines **156** resulted in the production of similar products **157** via an intramolecular Mannich reaction (**Scheme 53 Path B**).^[79]

Scheme 53



This type of nucleophilic addition/electrophilic trapping was also extended to include [2+3]-cycloadditions of nitrones **158** to provide isoxazolidines **159** in good yield and moderate diastereoselectivities (**Scheme 54**).^[80] Exposure of products **159** to zinc in acetic acid allowed for the reductive cleavage of the N-O bond and subsequent rearrangement to pyrrolines **160** and pyrroles **161**.

Scheme 54.

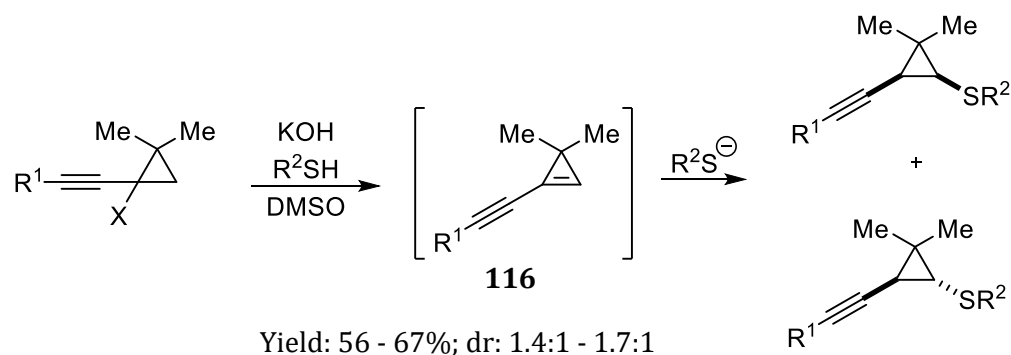


4.2.2 Addition of Sulfur Nucleophiles

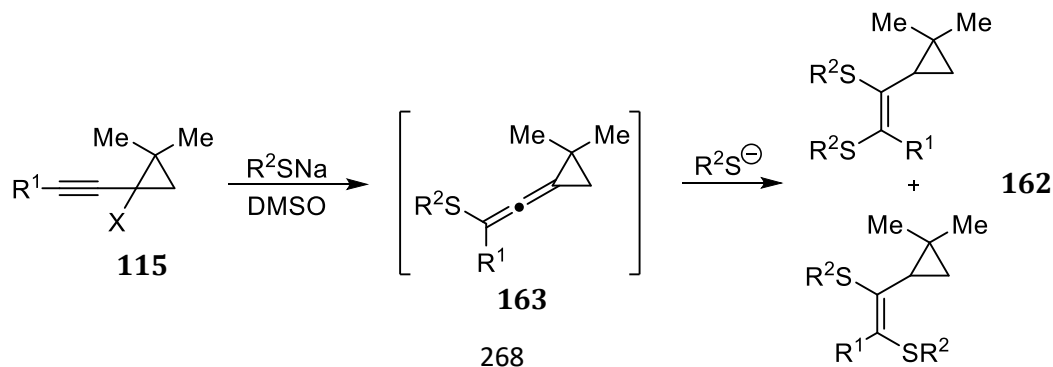
Thiols and thiophenolates are more reactive nucleophiles and stronger acids than their oxygen based analogs discussed in section 4.2.1. The increased reactivity has two repercussions including generally reduced stereoselectivity and requiring additional base loading to achieve proper effective basicity. Shavrin demonstrated that sulfur nucleophiles, just as oxygen nucleophiles in scheme 45, underwent conjugate addition to in-situ generated cyclopropene **116** but without diastereoselectivity (**Scheme 55a**).^[81] The reduced basicity of thiolates was demonstrated by exposure of cyclopropane **115** to sodium thiolate in DMSO which failed to undergo intended 1,2-dehydrohalogenation to form cyclopropene intermediate **116** (**Scheme 55b**).^[81] Instead, a mixture of *E*- and *Z*-configured olefin products **162** were obtained which were believed to result from the initial addition of thiolate to the triple bond to provide allene intermediate **163** followed by addition of another equivalent of thiolate to provide **162**.

Scheme 55

a)

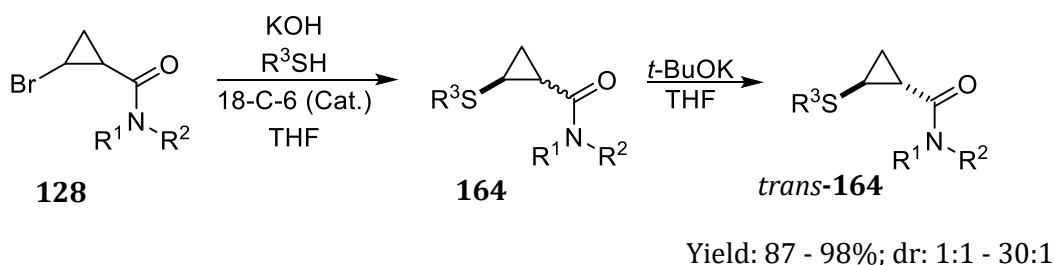


b)



Rubin has reported that thiolates and thiophenolates are efficient nucleophiles for conjugate addition to cyclopropenes generated from cyclopropyl bromide **128** (**Scheme 56**).^[72] These nucleophiles exhibited similarly poor diastereoselectivity in crude products **164** as was observed during addition of phenols in scheme 48. This observation was attributed to the decreased propensity for efficient epimerization in systems possessing relatively acidic nucleophilic components. As was previously shown during the addition of phenols, the diastereomeric ratio could greatly be improved by subjecting the crude mixture of *cis*- and *trans*-configured **164** to more basic conditions to selectively provide the thermodynamically favored *trans*-product **164**.

Scheme 56

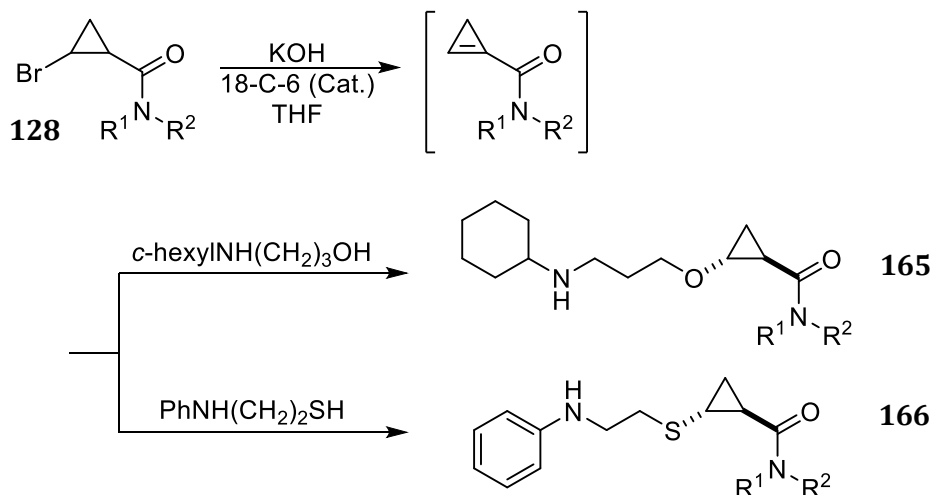


4.2.3 Addition of Nitrogen Nucleophiles

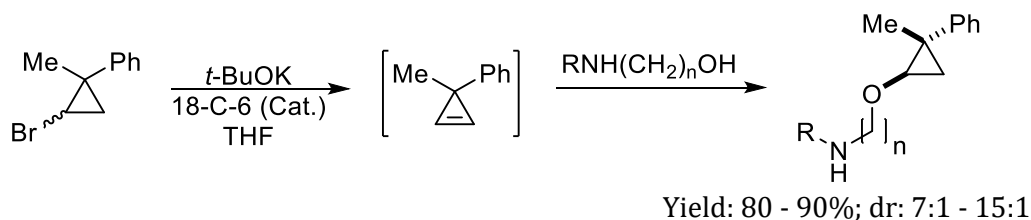
Competition experiments revealing the reactivity of nitrogen nucleophiles against alkoxides and thiolates were conducted by Rubin (**Scheme 57**).^[72,82] Both reactions conducted between cyclopropyl bromide **128** and bifunctional pronucleophiles led to exclusive production of products **165** and **166**. The high selectivity for oxygen- or sulfur- nucleophilic attack was rationalized by the particular deprotonation of the far more acidic alcohol or thiol under weakly basic reaction conditions.^[70]

Scheme 57

a)



b)

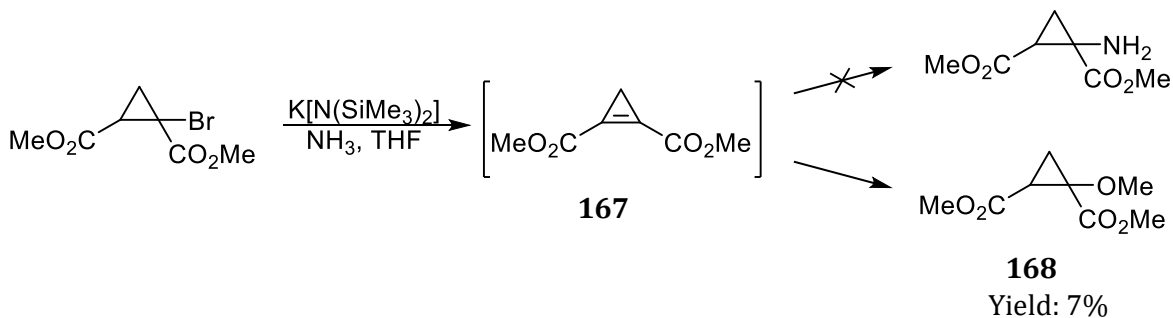


The relative poor nucleophilicity of nitrogen nucleophiles has been overcome by either utilizing a stronger base capable of efficiently deprotonating secondary amines or by incorporation of an electron-withdrawing group thus activating the N-H bond toward deprotonation by weaker bases.

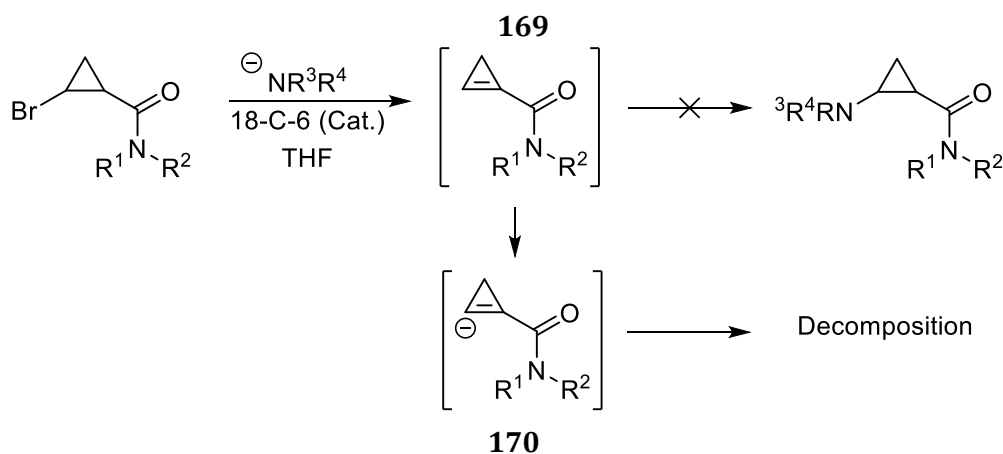
Taylor attempted to conduct the addition of ammonia to in-situ generated cyclopropene **167** using potassium hexamethyldisilazide as base (**Scheme 58**).^[83] This process was unsuccessful as methoxycyclopropane **168** was the only observed product in very poor yield. Rubin has also reported the failure of amide bases to undergo conjugate addition to cyclopropene **169**.^[82] It was proposed that instead of acting as a nucleophile the amide base deprotonates cyclopropene **169** to generate cyclopropene anion **170** which only led to decomposition (**Scheme 59**).^[82] Amide

bases were successfully added to alkynyl cyclopropenes **116** and **119** (Scheme 60a and 60b).^[84,85]

Scheme 58

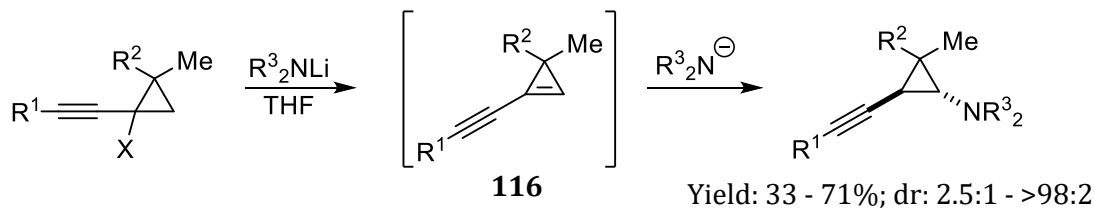


Scheme 59

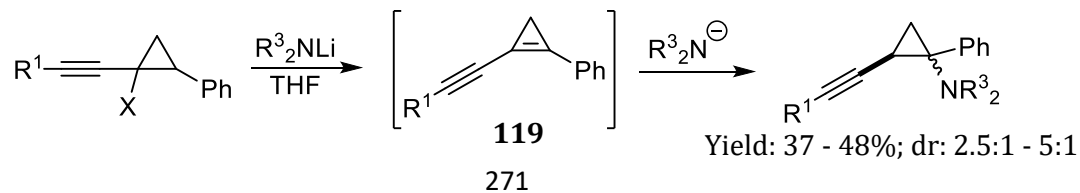


Scheme 60

a)



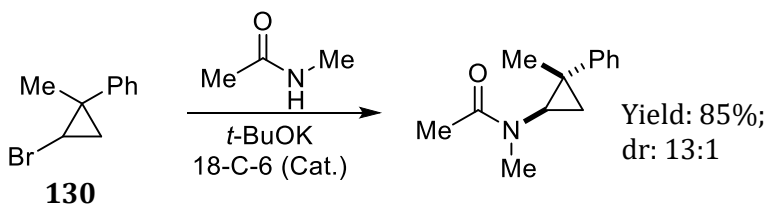
b)



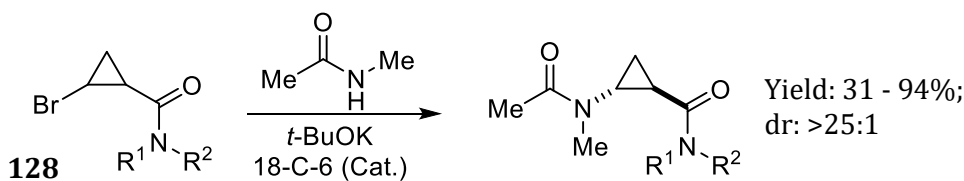
The strategy of utilizing nitrogen pronucleophiles with enhanced acidity was utilized by Rubin during the formal nucleophilic substitution of cyclopropyl bromide **130** with N-methylacetamide under steric control (**Scheme 61a**).^[82] Likewise, carboxamide and sulfonamide pronucleophiles were found to undergo addition to conjugated cyclopropenes formed from cyclopropanes **128** under thermodynamic control (**Scheme 61b** and **61c**).^[82] Azoles and anilines, which possess similar acidity as carboxamides, were also reported to undergo this transformation to provide N-substituted cyclopropanes **171** and **172** (**Scheme 62**).^[82] It is also possible to add nitrogen nucleophiles in the form of pyrroles and indoles to cyclopropenes under directed (**Scheme 63a**) and dual-control (**Scheme 63b**) methods.^[82]

Scheme 61

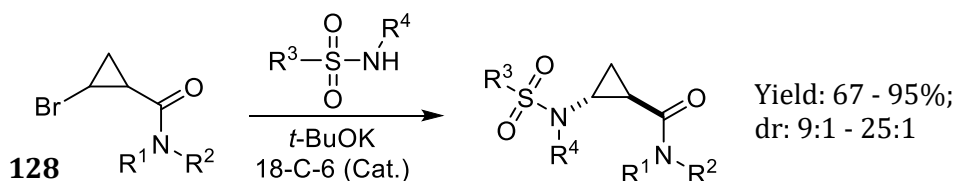
a)



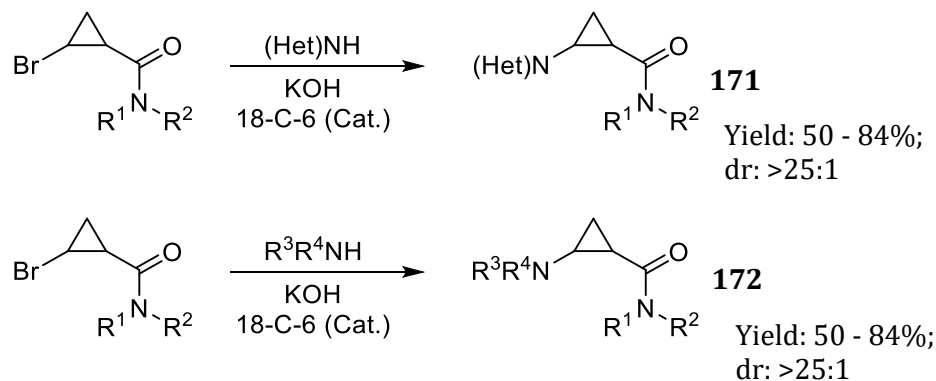
b)



c)

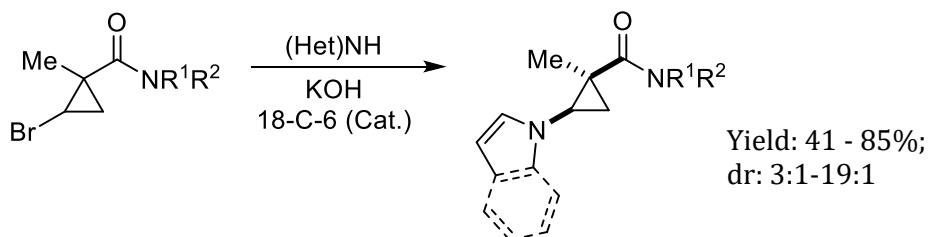


Scheme 62

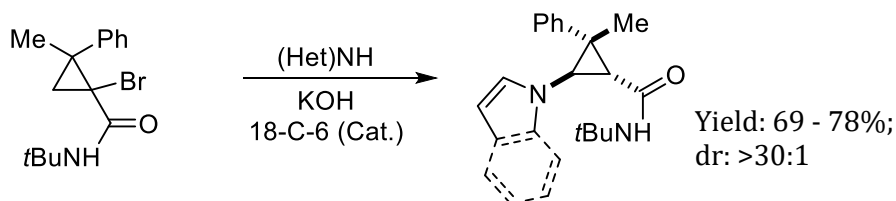


Scheme 63

a)



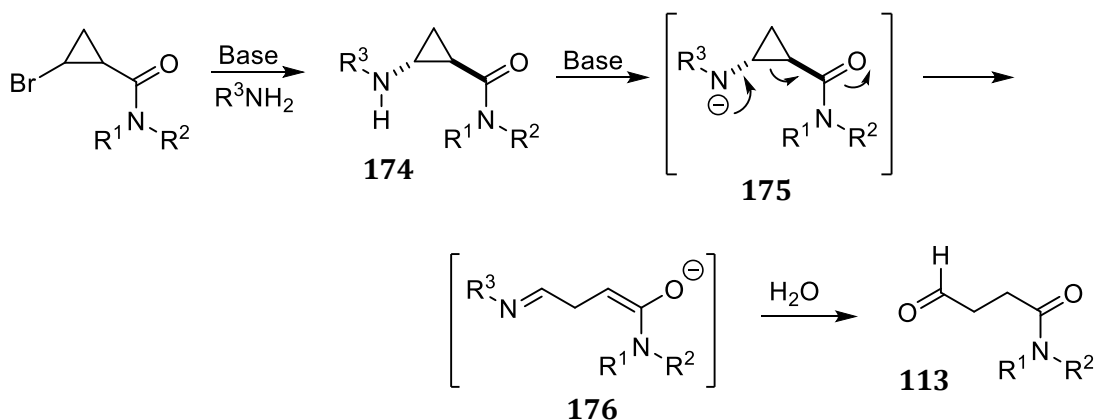
b)



It is important to note nucleophilic additions reported by Rubin were strictly limited to secondary nitrogen nucleophiles. All attempts to incorporate primary nitrogen nucleophiles resulted in the nucleophile-catalyzed ring-opening process to provide aldehyde **173** (**Scheme 64**).^[82] Initially the primary nitrogen nucleophile undergoes typical nucleophilic addition to cyclopropene to establish species **174**. The presence of an additional acidic N-H bond allowed for a second deprotonation to generate amide **175** which was followed by strain-release driven ring-

opening to form imine **176**. Subsequent exposure to aqueous conditions resulted in hydrolysis of the imine and formation of linear aldehyde **173** as the sole product

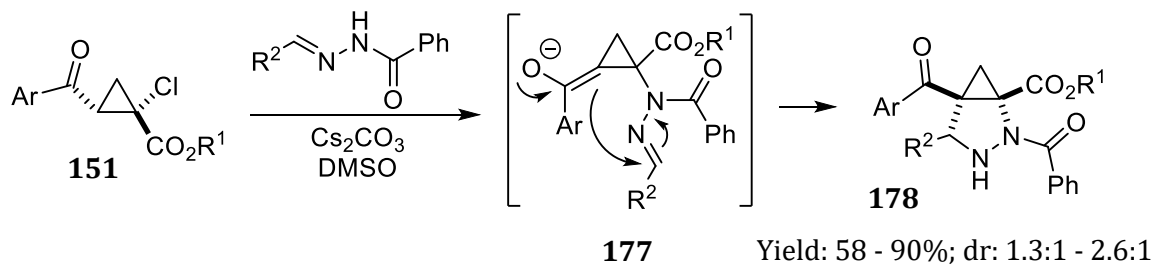
Scheme 64



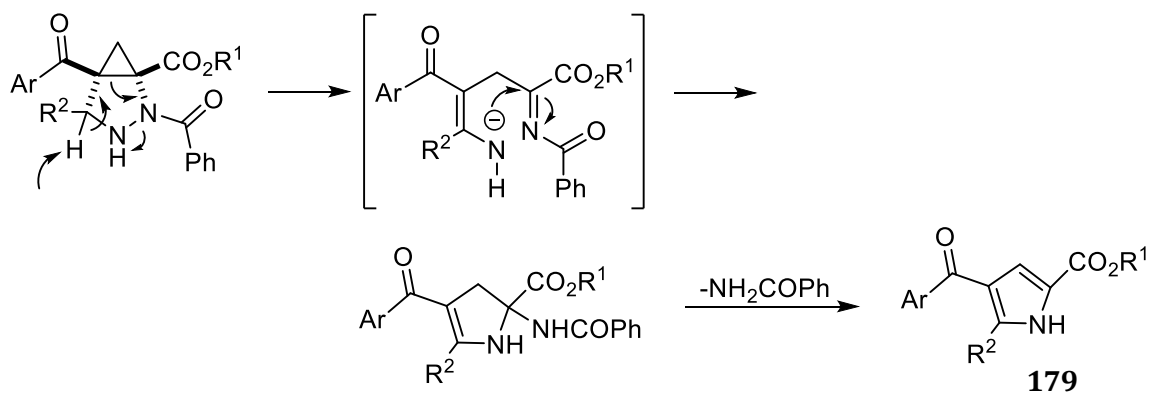
Gong has also demonstrated a nucleophilic addition/electrophilic trapping sequence using nitrogen nucleophiles similar to the chemistry previously shown with phenoxide nucleophiles (**Scheme 65a**).^[88] N-acylhydrazones were shown to undergo efficient addition to cyclopropenes generated from cyclopropyl chloride **151** to provide intermediate **177** which could react in an intramolecular mannich reaction yielding pyrazolidines **178**. The heating of products **178** under proper conditions resulted in ring opening and subsequent elimination of benzamide to provide pyrrole derivatives **179** (**Scheme 65b**).^[88] Additionally, the addition of secondary amides to cyclopropene **152** resulted in a ring-opening/ring-closure sequence to provide pyrones **180** (**Scheme 66**).^[89]

Scheme 65

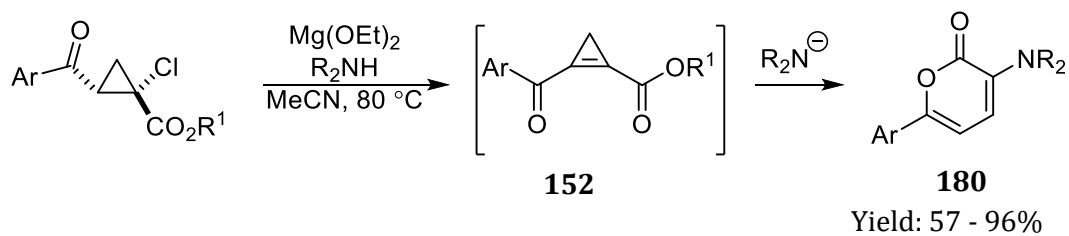
a)



b)

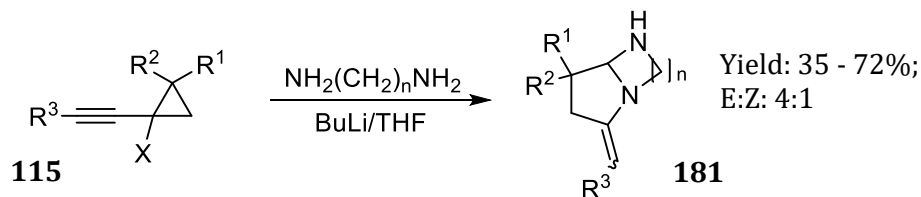


Scheme 66



Gvozdev reported the addition of primary diamines to alkynylcyclopropane **115** followed by a rearrangement to provide products **181** (Scheme 67).^[90,91]

Scheme 67



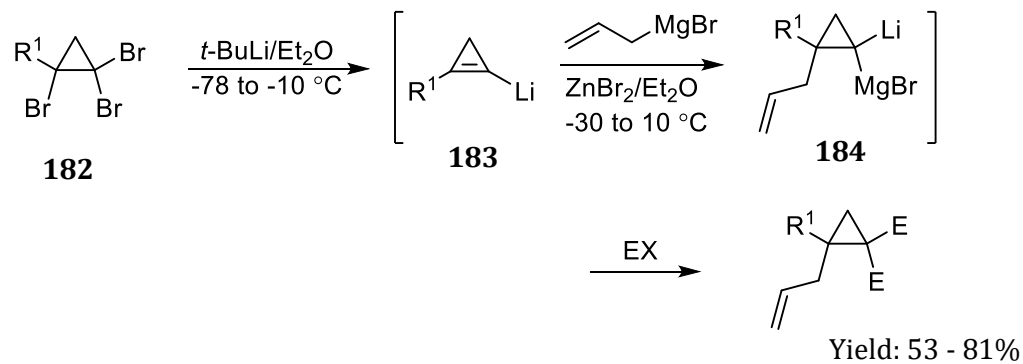
4.2.4 Addition of Carbon Nucleophiles

While the number of reports detailing the addition of carbon based nucleophiles to in-situ generated cyclopropenes is far fewer than what has been reported for additions to pre-generated cyclopropenes (see section 4.3.6), both organometallic reagents and enolates have been shown to display this type of reactivity. Marek reported tri-functionalization of cyclopropanes **182** via initial direct addition of allylmagnesium bromide to cyclopropenyl lithium species **183** to generate **184**. Subsequent exposure to two equivalents of an electrophilic component provided tetra-substituted cyclopropanes (**Scheme 68a**).^[92] Further development of this chemistry allowed for the diastereoselective incorporation of two non-identical electrophiles via the placement of a hydroxymethyl substituent at C-3 of **185**. (**Scheme 68b**).^[92] In species **186**, the first equivalent of an electrophilic quench is added in a *trans*-configuration to the directing group due to the stabilizing coordination between the alkoxide and metal cation.

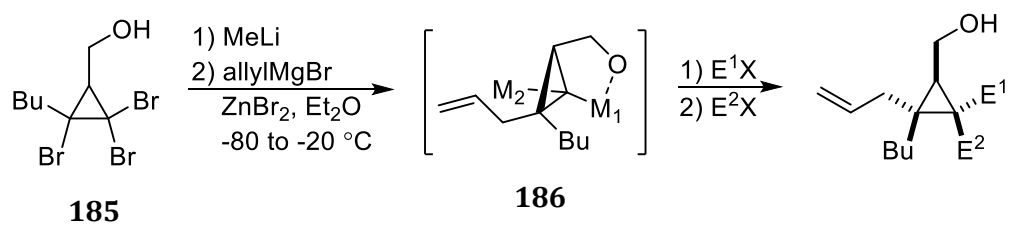
Gong has reported the nucleophilic addition of carbon based enolate nucleophiles to cyclopropanes **151** using 1,3-diketone pro-nucleophiles to provide cyclopropanes **187** which, under basic reaction conditions underwent subsequent rearrangement to fulvenes **188** (**Scheme 69**).^[93]

Scheme 68

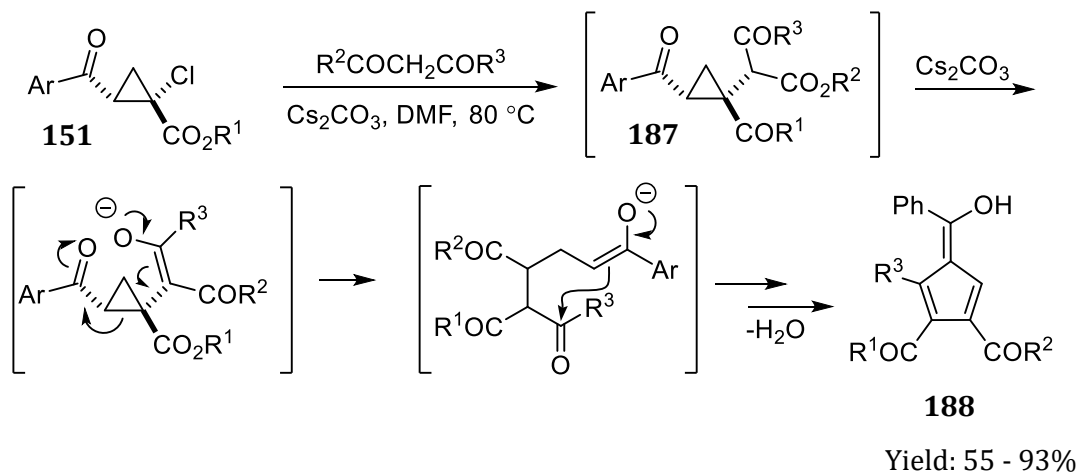
a)



b)



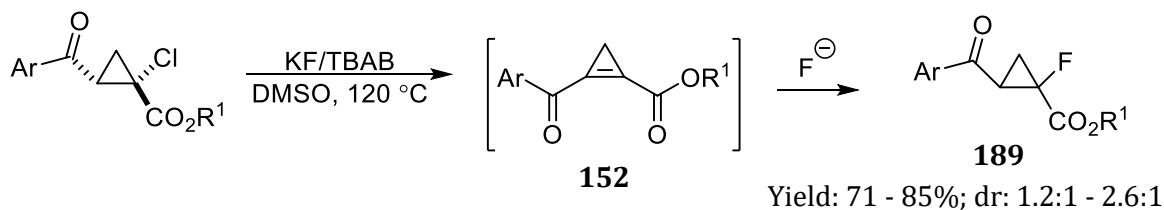
Scheme 69



4.2.5 Addition of Halogen Nucleophiles

Very recently, a single example demonstrating the ability of halogen nucleophiles to add to cyclopropenes has been reported. Gong demonstrated that fluoride underwent nucleophilic addition to cyclopropene **152** to provide fluorinated cyclopropane **189** (**Scheme 70**).^[95] The rather surprising formation of cyclopropene under such weakly basic conditions was confirmed via [4+2]-cycloaddition reaction with anthracene.

Scheme 70



4.3 Additions to Pre-Generated Cyclopropenes

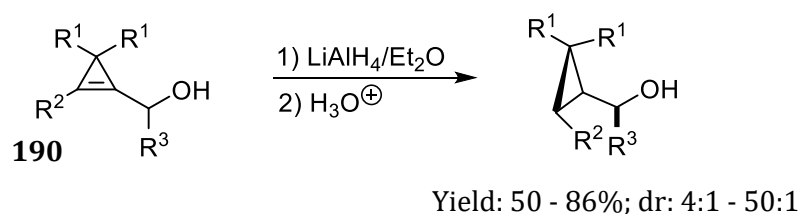
Stable cyclopropenes which can be isolated in pure form offer more general reactivity and less restrictive reaction conditions than those generated in-situ. However, the requirement of isolable cyclopropenes to resist decomposition limits the substitution pattern around the ring to those which possess proper stabilization (**Figure 8**). Thus, additions to pre-generated cyclopropenes often require harsher conditions to achieve the desired reactivity which may cause complications with stereoselectivity. Despite these concerns, reactions involving the addition of hydride, oxygen, sulfur, nitrogen, phosphorus, and carbon nucleophiles to pre-generated cyclopropenes have been reported.

4.3.1 Addition of Hydride Nucleophiles

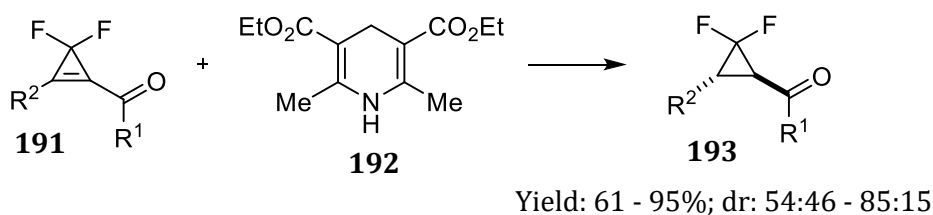
The reduction of cyclopropenes to cyclopropanes using hydride sources such as lithium aluminum hydride has been known for over 50 years.^[96-98] However, not until recently has the

stereoselective addition of such nucleophiles been observed. Marek has shown that cyclopropene **190** underwent diastereoselective reduction via efficient coordination between the incoming nucleophilic species and the alkoxide directing group (**Scheme 71**).^[100] Organic hydride sources can also be used to reduce cyclopropene as was demonstrated by the reduction of conjugated cyclopropene **191** with Hantzsch ester **192** to provide cyclopropane **193** with moderate diastereoselectivity (**Scheme 72**).^[101] Hydride nucleophiles delivered in a catalytic fashion is also known. Marek reported the production of methylene cyclopropane **194** via catalytic S_N2' addition of hydride to cyclopropene **195** (**Scheme 73**).^[102]

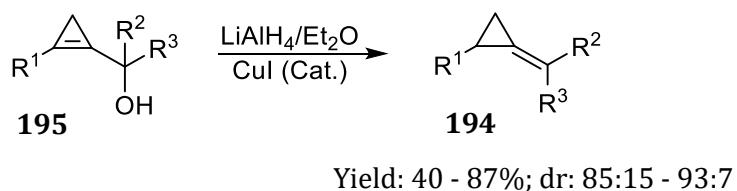
Scheme 71



Scheme 72



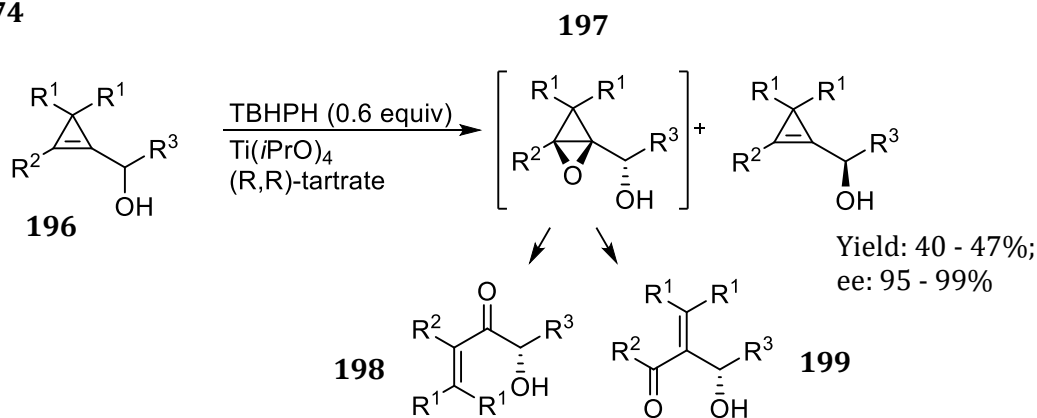
Scheme 73



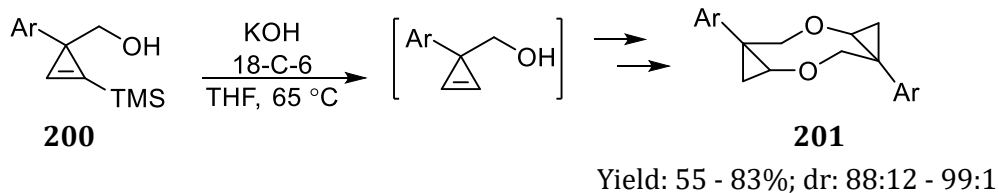
4.3.2 Addition of Oxygen Nucleophiles

The addition of oxygen nucleophiles to cyclopropenes often occurs under conditions facilitating efficient 1,2-dehydrobromination and therefore is more commonly conducted with in-situ generated cyclopropenes (See section 4.2.1). However, pre-generated cyclopropenes offer the advantage of being less prone to decomposition and therefore provide a possibility for the addition of very weak nucleophiles which require harsher conditions and longer reaction times to achieve acceptable yield. Sharpless epoxidation was used for the kinetic resolution of racemic cyclopropene **196** (Scheme 74).^[103,104] In this system, one enantiomer of **196** underwent epoxidation to species **197**, which subsequently decomposed to products **198** and **199** while the other enantiomer of **196** failed to react and remained intact. Recently, Rubin has reported the addition of primary alkoxides to pre-generated cyclopropenes. In this instance **200** underwent dimerization to generate 8-membered 1,5-dioxocanes **201** in a highly diastereoselective manner (Scheme 75).^[107] A [3,3]-sigmatropic rearrangement has been reported with pre-generated cyclopropene **202** (Scheme 76).^[104,108]

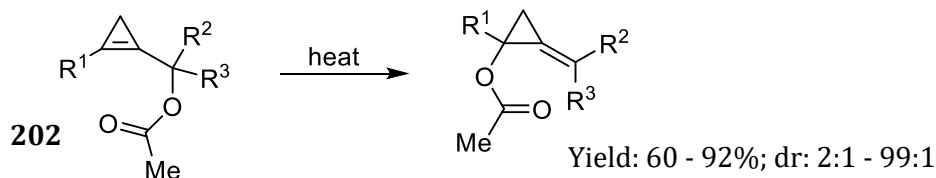
Scheme 74



Scheme 75



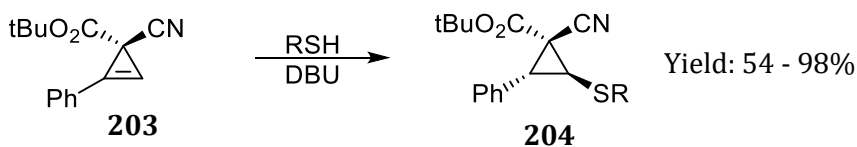
Scheme 76



4.3.3 Addition of Sulfur Nucleophiles

Zhang demonstrated that sulfur nucleophiles are compatible in nucleophilic additions to pre-generated cyclopropenes. He showed that optically active cyclopropene **203**, obtained from asymmetric cyclopropenation of phenylacetylene, undergoes highly regioselective formation of cyclopropane **204** with complete conservation of optical purity (**Scheme 77**).^[109]

Scheme 77

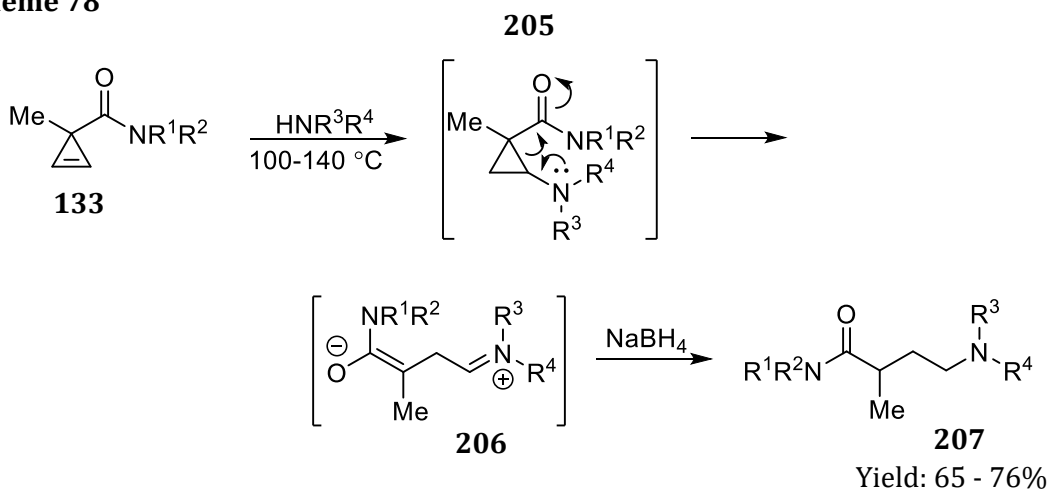


4.3.4 Addition of Nitrogen Nucleophiles

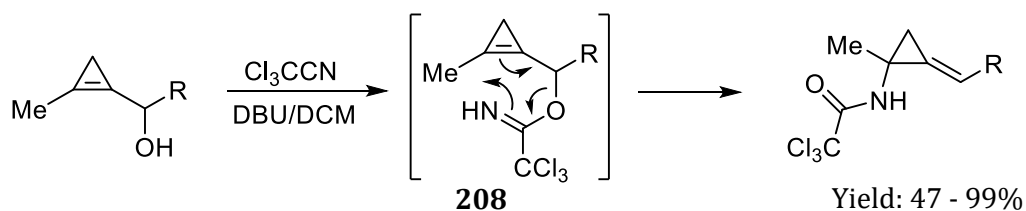
Despite the relatively high nucleophilicity of amine nucleophiles, very few examples of their nucleophilic addition to cyclopropenes have been reported. This has been attributed to their decreased acidity which, in reactions with in-situ generated cyclopropenes resulted in their out-competition by alkoxide and thiolate nucleophiles. Recently, Rubin showed that by employing

pre-generated cyclopropenes this obstacle could be overcome (**Scheme 78**).^[110] Exposure of cyclopropene **133** to secondary amines at elevated temperatures generated push-pull aminocyclopropane **205**. Following ring-opening, zwitterionic species **206** could be efficiently reduced to provide GABA derivatives **207**. Additionally, Hyland reported a [3,3]-sigmatropic rearrangement of cyclopropene intermediates **208** (**Scheme 79**).^[111]

Scheme 78



Scheme 79

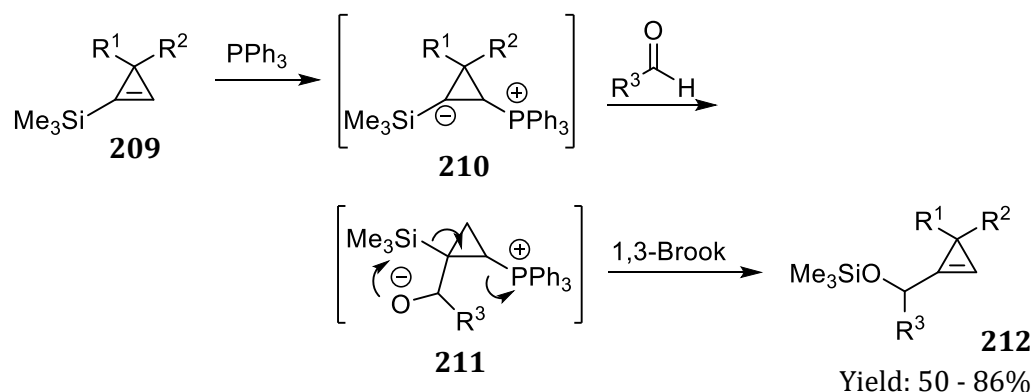


4.3.5 Addition of Phosphorus Nucleophiles

The direct nucleophilic addition of phosphorous nucleophiles to cyclopropenes remains largely unknown, although it was proposed to occur catalytically by Gevorgyan in the development of the Morita-Baylis-Hillman reaction of cyclopropenes (**Scheme 80**).^[113] It was reasoned that nucleophilic attack of triphenylphosphine at the less sterically hindered site of

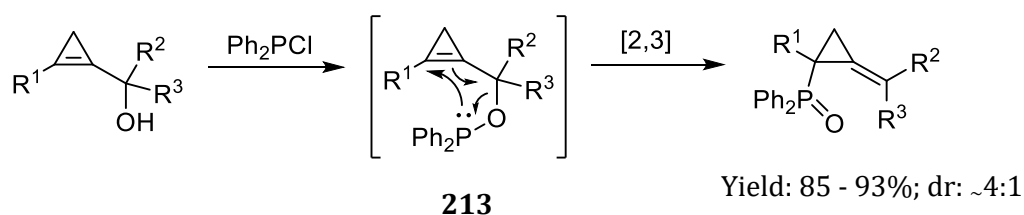
cyclopropene **209** would lead to stabilized zwitterionic intermediate **210**. Introduction of an aldehyde to the reaction resulted in formation of species **211** which, then underwent a 1,3-Brook rearrangement to reform cyclopropene **212** and expel triphenylphosphine.

Scheme 80



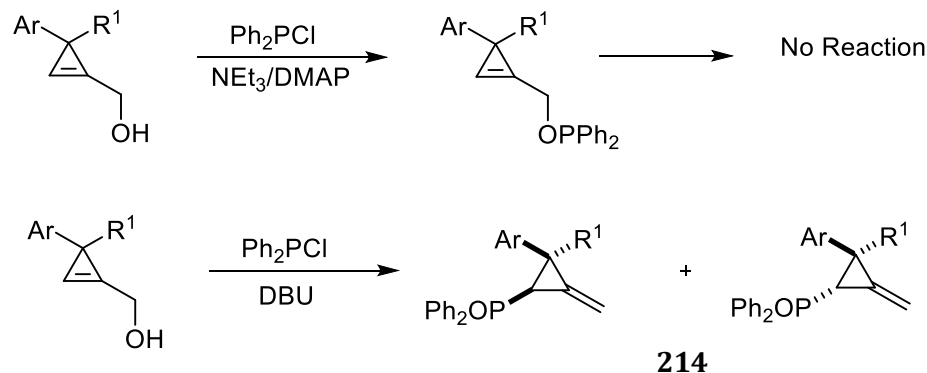
Marek has reported the [2,3]-sigmatropic rearrangement of cyclopropene intermediates **213** (**Scheme 81**).^[108] This reactivity is similar to sigmatropic rearrangements reported in the addition of oxygen (**Scheme 76**) and nitrogen (**Scheme 79**) nucleophiles.

Scheme 81



Nearly simultaneously, Rubin reported the synthesis of cyclopropene phosphonates **214** (**Scheme 82**).^[114] Interestingly, this reaction was found to occur only in the presence of the Lewis base DBU and to provide opposite diastereoselectivity based on the identity of the aryl substituent.

Scheme 82



Yield: 47 - 96%; dr: 5.2:1 - 1.3:1

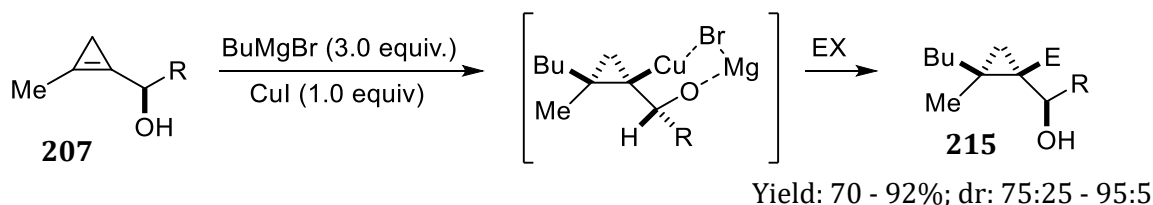
4.3.6 Addition of Carbon Nucleophiles

The direct addition of organometallic reagents to cyclopropenes has been known for more than 50 years and was detailed by Fox in a 2005 review.^[115] Recently, the catalytic delivery of organometallic carbon nucleophiles has begun to receive considerable attention. Reports on the direct and catalytic addition of organometallic reagents to pre-generated cyclopropenes dating to post-2005 are detailed in this section.

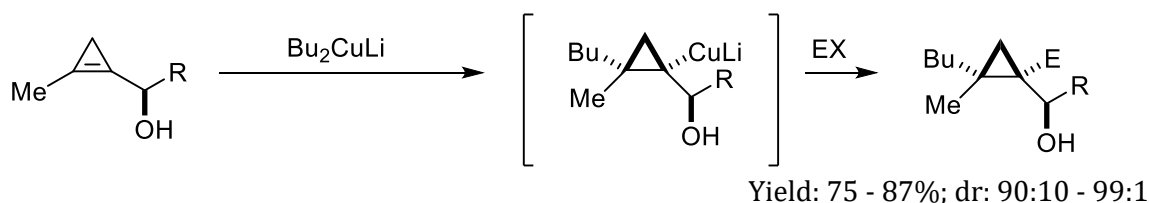
Marek First described the copper-mediated delivery of Grignard reagents to pre-generated cyclopropenes **207** to provide difunctionalized cyclopropane products **215** in which diastereoselectivity was determined by efficient coordination with the hydroxymethyl directing group (**Scheme 83a**).^[119] Interestingly, he reported that facial selectivity was dependent on the identity of the organocopper species and utilization of stoichiometric Gilman cuprate resulted in opposite diastereoselectivity (**Scheme 83b**).^[119]

Scheme 83

a)

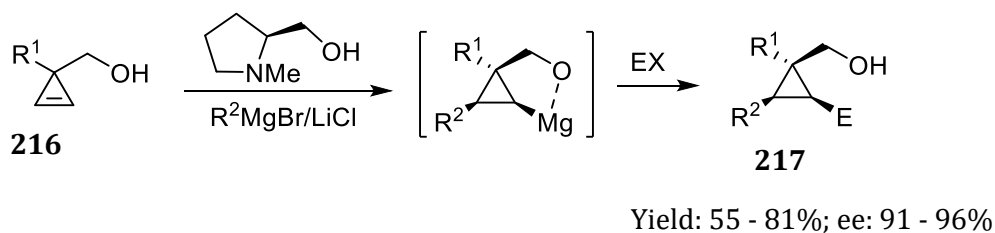


b)



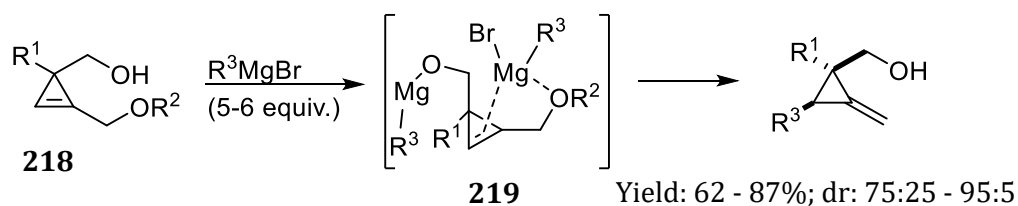
A highly diastereo- and enantioselective direct addition of Grignard reagents to cyclopropene **216** has been reported which uses (*S*)-*N*-methylprolinol to provide cyclopropane **217** in high enantiomeric ratios (**Scheme 84**).^[123] Fox reported a similar diastereoselective direct addition of Grignard reagents to cyclopropenes **218** (**Scheme 85a**).^[124] The use of 5-6 equivalents of Grignard reagent to achieve this transformation was justified via proposition of intermediate **219** in which two equivalents of RMgBr were required to properly activate the double bond toward nucleophilic addition. One equivalent was proposed to coordinate to the alkoxide directing group and act as the nucleophile in the reaction while the second equivalent would act as a Lewis acid and activate the leaving group. Recently, the catalytic delivery of Grignard reagents to 1-hydroxymethylcyclopropene **207** has been described by Marek. Interestingly, the catalytic transformation proceeded by an S_N2'-type mechanism to provide methylene cyclopropanes **220**, which is different than what was reported in the stoichiometric reaction shown in scheme 83 (**Scheme 85b**).^[104]

Scheme 84

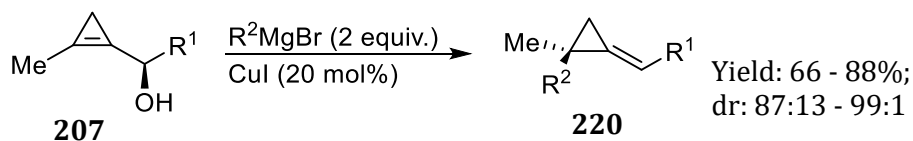


Scheme 85

a)



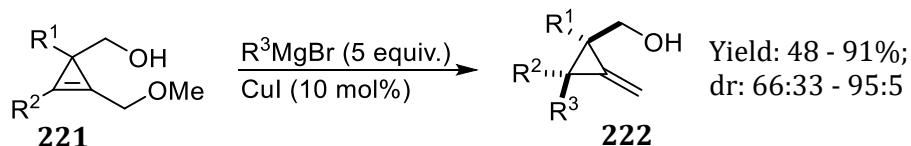
b)



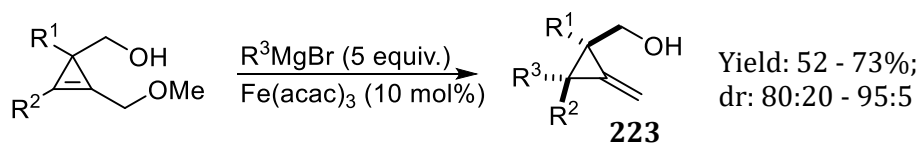
Catalytic allylic transposition of cyclopropenes **221** has also been achieved. Interestingly, it was found that different facial selectivities could be achieved by using different catalysts. The reaction proceeded under directed control by use of a copper catalyst to provide *cis*-configured methylene cyclopropane **222** (Scheme 86a),^[125] and under steric control to *trans*-configured product **223** with an iron catalyst (Scheme 86b).^[125]

Scheme 86

a)



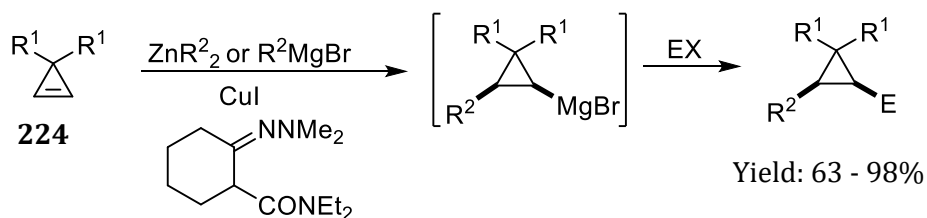
b)



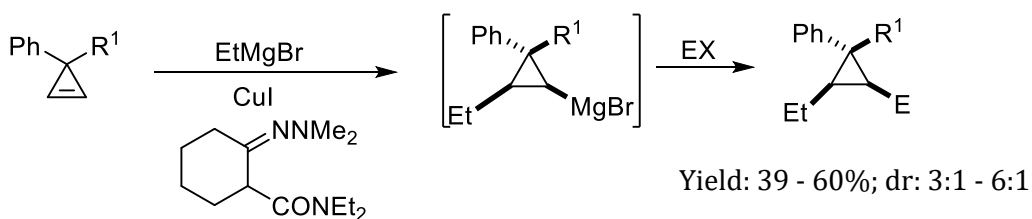
Recently catalytic carbomagnesiation and carbozincation reaction of 3,3-disubstituted cyclopropenes have also been developed. Endo first described the copper-catalyzed carbomagnesiation and carbocupration of symmetric cyclopropene **224** using a hydrazine-carboxamide ligand (**Scheme 87a**).^[126] Further attempts to achieve facial selectivity under steric control only provided marginal diastereoselectivity (**Scheme 87b**).^[126]

Scheme 87

a)



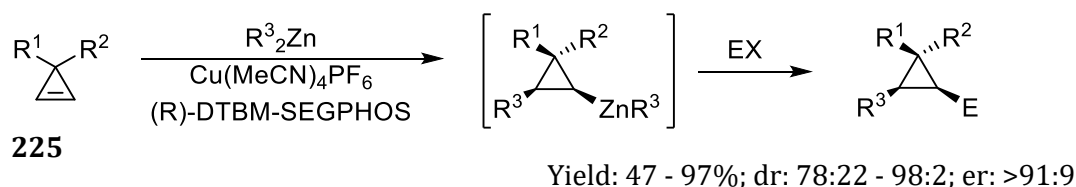
b)



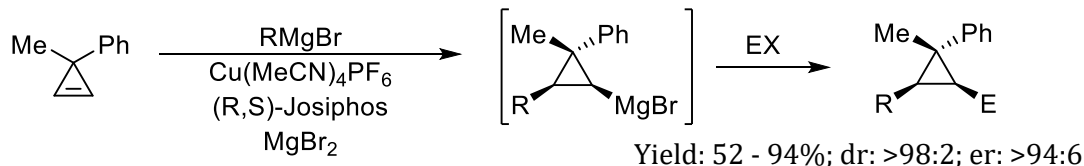
A major development was reported by Marek when he reported the copper-catalyzed asymmetric carbozincation of cyclopropenes **225**. In this reaction the steric influence of the substituents at C-3 of **225** resulted in good facial selectivity while efficient enantioselectivity was established by a chiral SEGPHOS ligand (**Scheme 88a**).^[127] In 2017, this work was extended to include asymmetric carbomagnesiation using (R,S)-Josiphos ligand (**Scheme 88b**).^[128]

Scheme 88

a)



b)

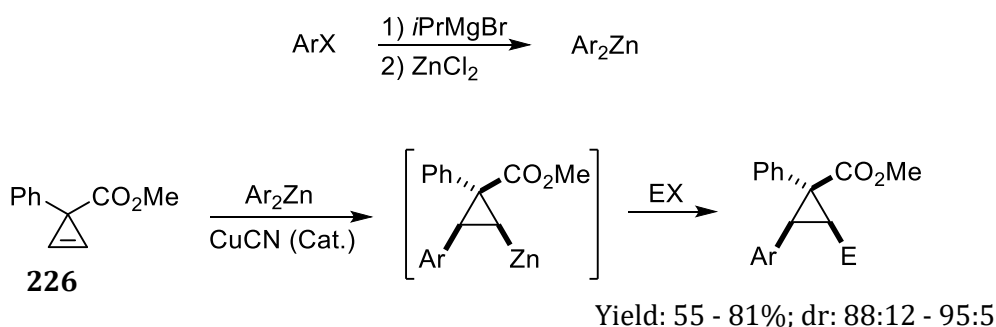


The directed catalytic asymmetric addition of organometallic reagents to 3-substituted cyclopropenes remains unknown, most probably due to the susceptibility of intermediate cyclopropane structures bearing electron-withdrawing directing groups to undergo ring-opening. Furthermore, the exposure of carbonyl-based directing groups to excess organometallic reagents often requires extreme cooling to prevent unwanted decomposition.

Fox conducted investigations concerning the catalytic carbozincation of cyclopropene **226** utilizing an ester functionality at C-3 as an efficient directing group (**Scheme 89**).^[121] In this process organozinc reagents were prepared prior to introduction to the carbozincation reaction

by exposure of various aryl halides first to isopropylmagnesium bromide and then zinc(II) chloride in 1,4-dioxane. It was found that reactions carried out in diethyl ether resulted in reduced facial selectivity which, was postulated to be due to the presence of Lewis acidic magnesium salts. Incorporation of 1,4-dioxane as a co-solvent eliminated this problem and diastereoselectivities improved in all examples.

Scheme 89



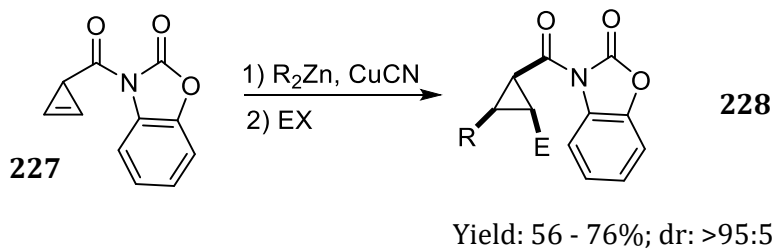
Oxazolidinone auxiliaries have also been shown to be highly efficient directing groups for the copper mediated carbozincation of cyclopropene **227** providing *cis*-configured tri-substituted cyclopropanes **228** with a high degree of diastereoselectivity (**Scheme 90a**).^[120] Additionally, carbozincation of cyclopropene **229** bearing chiral oxazolidinone auxiliary allowed for the production of products **230** possessing three contiguous stereocenters (**Scheme 90b**).

[123]

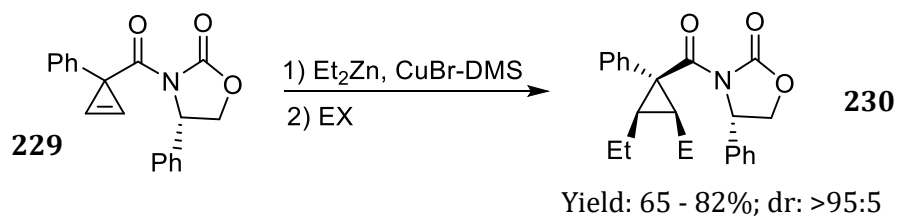
Marek has described the copper-catalyzed addition of Grignard reagents to optically active cyclopropenes **231** to form intermediate **232** which underwent facile oxidation under aerobic conditions. Subsequent ring-opening then produced enantioenriched aldehydes **233** (**Scheme 91a**).^[129] Interestingly, the use of stoichiometric cyanocuprate nucleophiles was able to provide the opposite configuration of **233** (**Scheme 91b**).^[129]

Scheme 90

a)

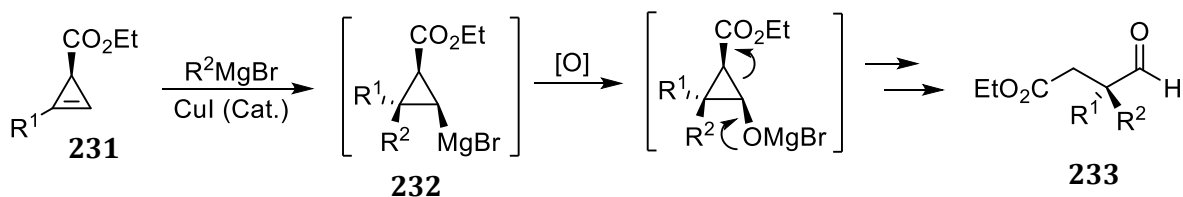


b)

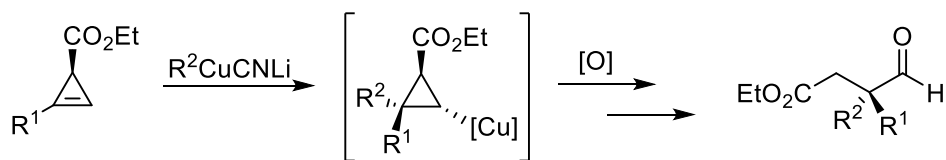


Scheme 91

a)



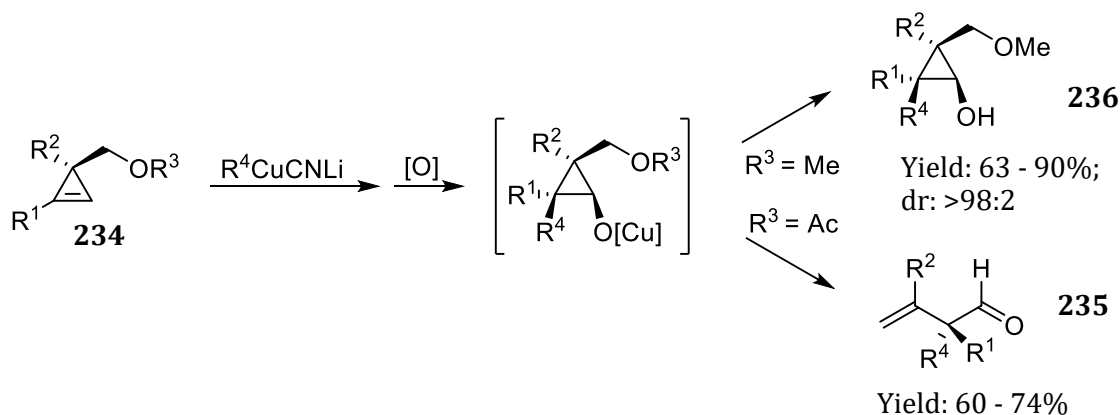
b)



A similar example showcased the highly variable stability of optically active cyclopropenes **234** possessing ester and ether directing groups (**Scheme 92**).^[130] Substrates bearing an acetoxymethyl function underwent complete ring opening to provide enantioenriched aldehyde

235. The presence of a methoxymethyl directing group at C-3 of **234** proved to be stabilized toward ring-opening and provided cyclopropanols **236**.

Scheme 92

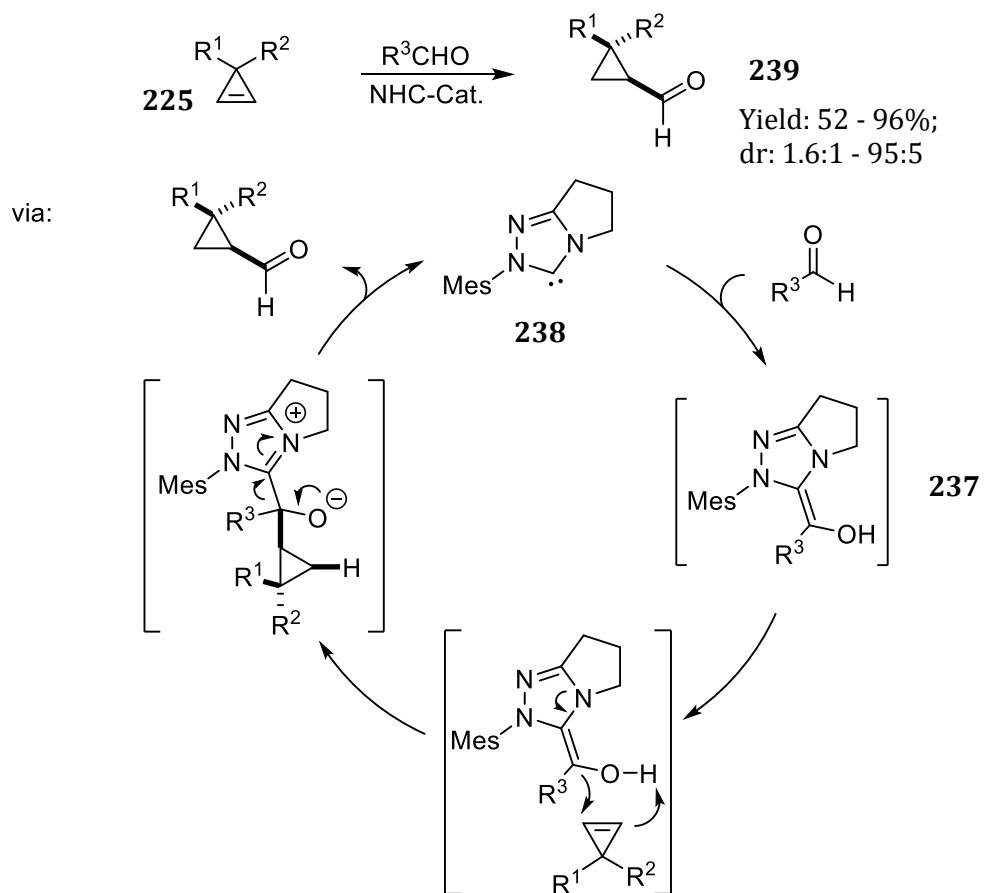


The Stetter reaction of cyclopropene **225** has been reported by Glorius which, was proposed to proceed via nucleophilic addition of Breslow intermediate **237** to cyclopropene **225** under steric control (**Scheme 93a**).^[133] Subsequent formation of an aldehyde would return species **238** to the catalytic cycle and provide cyclopropane **239**. An asymmetric version of this chemistry has also been developed using chiral catalyst **240** (**Scheme 93b**).^[135]

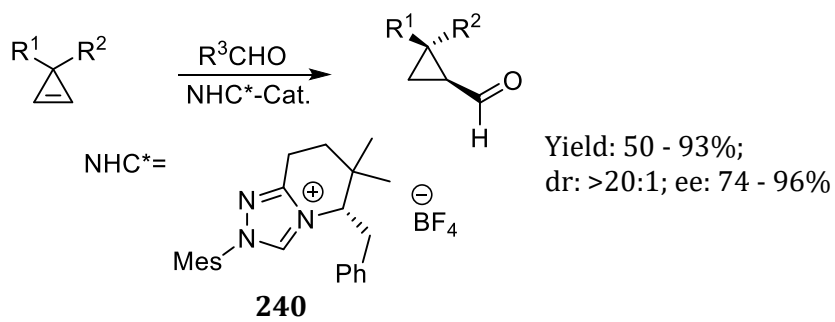
Meyer and Cossy have reported a diastereoselective Ireland-Claisen rearrangement of cyclopropenes **241** (**Scheme 94**).^[138] It was proposed that exposure of **241** to basic conditions resulted in the formation of silyl enol ether intermediate **242**. Next, a strain-release driven [3,3]-sigmatropic rearrangement provided the observed products **243** with great diastereoselectivity.

Scheme 93

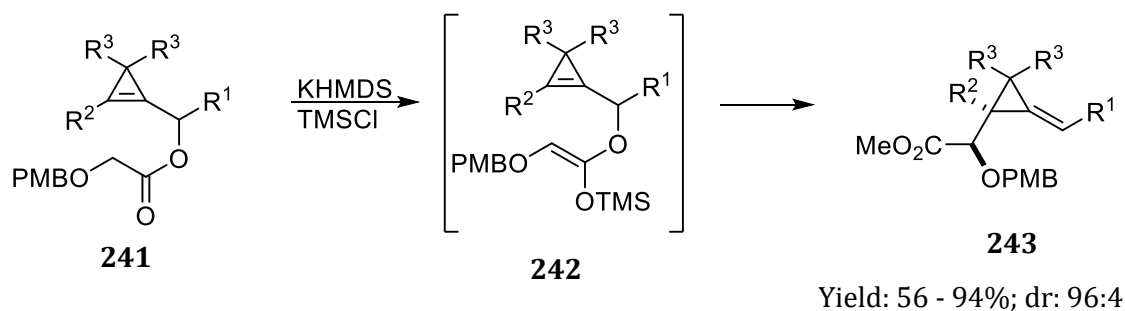
a)



b)



Scheme 94



4.4 Conclusion

The nucleophilic addition of heteroatom and carbon based nucleophiles has seen considerable development within the past decade. The use of strategically designed cyclopropene substrates and asymmetric catalysts has allowed for the development of a variety of highly diastereo- and enantioselective reactions under steric, thermodynamic, and directed control. The stereoselective construction of highly variable cyclopropane scaffolds offer interesting possibilities for biologically active small molecules. The tunable reactivity of many cyclopropane intermediates toward highly diastereoselective ring opening provide the possibility of using stereoselective nucleophilic additions to cyclopropenes as a vehicle for the synthesis of other complex cyclopropane lacking molecular structures.

Appendix

A-1) Xray Data for [21g]

Figure 9. ORTEP drawing of **21g** showing 50% probability amplitude displacement ellipsoids.

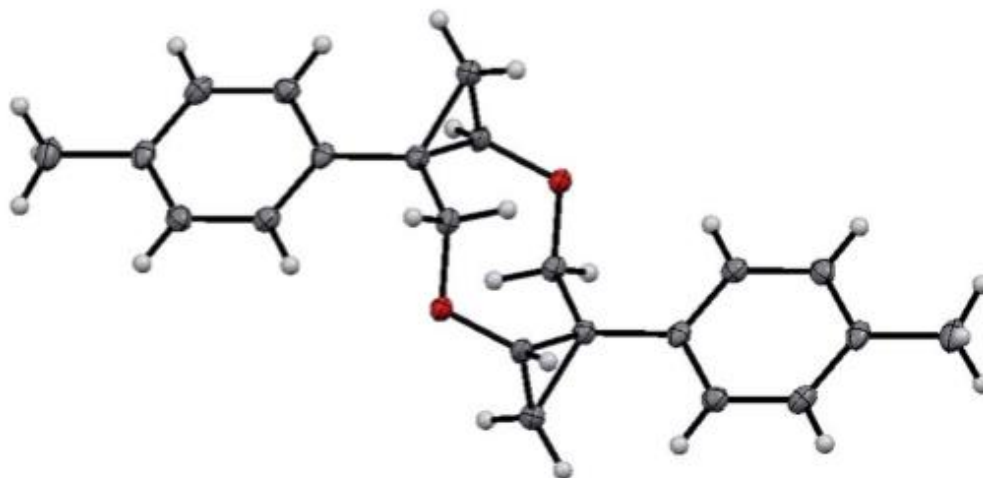


Figure 10. Packing of **21g** molecules in the crystalline lattice.

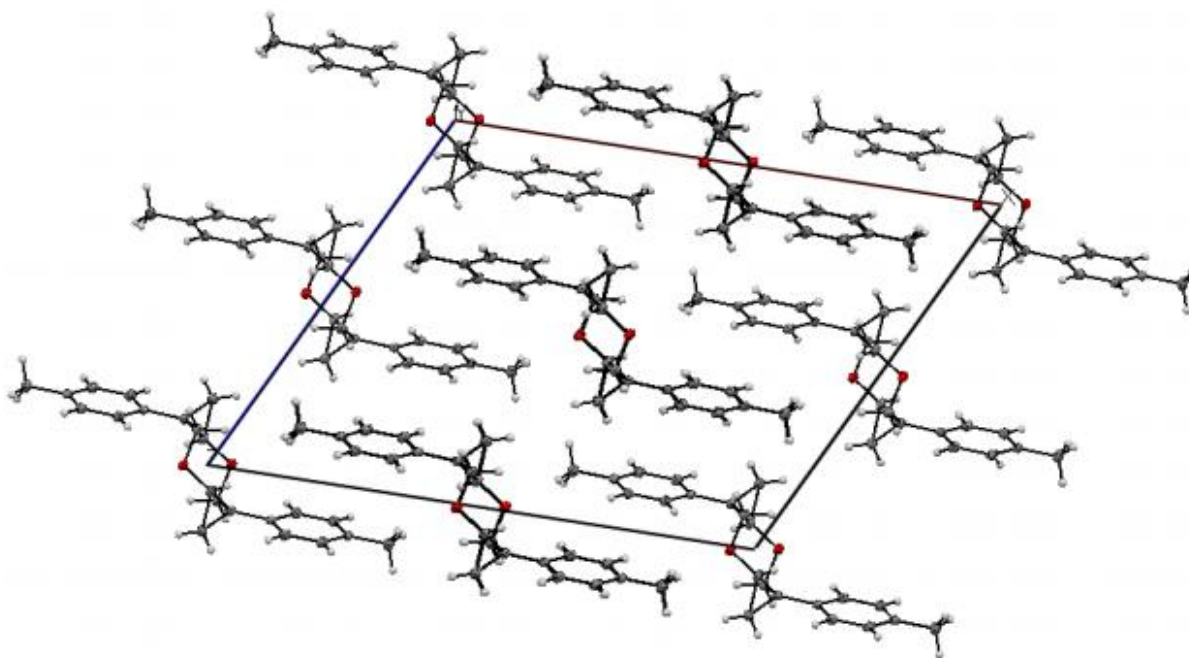


Table 31. Crystal data and structure refinement for **21g**.

Identification code	q32c	
Empirical formula	C ₂₂ H ₂₄ O ₂	
Formula weight	320.41	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.9651(7) Å	α = 90°
	b = 6.1398(2) Å	β = 116.9270(10)°
	c = 15.2881(6) Å	γ = 90°
Volume	1670.87(10) Å ³	
Z	4	
Density (calculated)	1.274 g/cm ³	
Absorption coefficient	0.623 mm ⁻¹	
F(000)	688	
Crystal size	0.30 x 0.08 x 0.04 mm ³	
Theta range for data collection	4.97 to 69.35°	
Index ranges	-22 ≤ h ≤ 23, -7 ≤ k ≤ 6, -18 ≤ l ≤ 16	
Reflections collected	7532	
Independent reflections	1507 [R(int) = 0.0163]	
Completeness to theta = 66.00°	98.4 %	
Absorption correction	Multi-scan	
Max and min transmission	1.000 and 0.873	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	1507 / 0 / 157	
Goodness-of-fit on F ²	1.054	
Final R indices [I > 2σ(I)]	R1 = 0.0347, wR2 = 0.0941	
R indices (all data)	R1 = 0.0349, wR2 = 0.0944	
Largest diff. peak and hole	0.274 and -0.186 e.Å ⁻³	

Table 32. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **21g**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	X	Y	Z	U(eq)
O	4600(1)	-2172(1)	5110(1)	16(1)
C(1)	4414(1)	-1542(2)	4114(1)	16(1)
C(2)	4079(1)	713(2)	3894(1)	15(1)
C(3)	4630(1)	2599(2)	4321(1)	16(1)
C(4)	4316(1)	2121(2)	3255(1)	19(1)
C(5)	3307(1)	1001(2)	3818(1)	15(1)
C(6)	2910(1)	2956(2)	3487(1)	18(1)
C(7)	2204(1)	3230(2)	3443(1)	19(1)
C(8)	1861(1)	1569(2)	3715(1)	19(1)
C(9)	2253(1)	-382(2)	4038(1)	19(1)
C(10)	2963(1)	-662(2)	4093(1)	17(1)
C(11)	1095(1)	1880(2)	3665(1)	25(1)

Table 33. Bond lengths [Å] and angles [°] for **21g**.

O-C(3)#1	1.4053(13)	C(3)#1-O-C(1)	112.89(8)
O-C(1)	1.4477(13)	O-C(1)-C(2)	110.89(9)
C(1)-C(2)	1.5076(15)	O-C(1)-H(1A)	108.4(8)
C(1)-H(1A)	0.991(13)	C(2)-C(1)-H(1A)	110.9(7)
C(1)-H(1B)	0.977(14)	O-C(1)-H(1B)	109.4(7)
C(2)-C(5)	1.5020(14)	C(2)-C(1)-H(1B)	110.7(8)
C(2)-C(3)	1.5258(15)	H(1A)-C(1)-H(1B)	106.4(11)
C(2)-C(4)	1.5325(15)	C(5)-C(2)-C(1)	117.50(9)
C(3)-O#1	1.4053(13)	C(5)-C(2)-C(3)	117.38(9)
C(3)-C(4)	1.4866(15)	C(1)-C(2)-C(3)	116.12(9)
C(3)-H(3)	0.965(15)	C(5)-C(2)-C(4)	119.12(9)
C(4)-H(4A)	0.974(15)	C(1)-C(2)-C(4)	115.20(9)
C(4)-H(4B)	0.946(15)	C(3)-C(2)-C(4)	58.17(7)
C(5)-C(10)	1.3978(16)	O#1-C(3)-C(4)	116.16(10)
C(5)-C(6)	1.4004(16)	O#1-C(3)-C(2)	119.86(9)
C(6)-C(7)	1.3907(16)	C(4)-C(3)-C(2)	61.14(7)
C(6)-H(6)	0.964(15)	O#1-C(3)-H(3)	114.8(8)
C(7)-C(8)	1.3922(18)	C(4)-C(3)-H(3)	119.1(8)
C(7)-H(7)	0.942(16)	C(2)-C(3)-H(3)	115.5(8)
C(8)-C(9)	1.3930(17)	C(3)-C(4)-C(2)	60.69(7)
C(8)-C(11)	1.5088(15)	C(3)-C(4)-H(4A)	118.6(8)
C(9)-C(10)	1.3928(16)	C(2)-C(4)-H(4A)	118.5(9)
C(9)-H(9)	0.965(15)	C(3)-C(4)-H(4B)	114.7(8)
C(10)-H(10)	0.975(15)	C(2)-C(4)-H(4B)	114.5(8)
C(11)-H(11A)	0.96(2)	H(4A)-C(4)-H(4B)	117.6(12)
C(11)-H(11C)	0.97(2)	C(10)-C(5)-C(2)	121.10(10)
C(11)-H(11B)	0.96(2)	C(10)-C(5)-C(6)	117.41(10)
C(6)-C(5)-C(2)	121.48(10)	C(7)-C(6)-H(6)	118.7(8)
C(7)-C(6)-C(5)	121.10(11)	C(5)-C(6)-H(6)	120.2(8)
C(6)-C(7)-C(8)	121.44(11)	C(9)-C(10)-C(5)	121.11(10)
C(6)-C(7)-H(7)	119.2(9)	C(9)-C(10)-H(10)	119.9(8)
C(8)-C(7)-H(7)	119.4(9)	C(5)-C(10)-H(10)	119.0(8)
C(7)-C(8)-C(9)	117.56(10)	C(8)-C(11)-H(11A)	112.4(12)
C(7)-C(8)-C(11)	121.10(11)	C(8)-C(11)-H(11B)	110.8(12)
C(9)-C(8)-C(11)	121.33(11)	H(11A)-C(11)-H(11B)	106.6(17)
C(10)-C(9)-C(8)	121.37(11)	C(8)-C(11)-H(11C)	111.0(12)
C(10)-C(9)-H(9)	119.1(8)	H(11A)-C(11)-H(11C)	104.5(17)
C(8)-C(9)-H(9)	119.5(8)	H(11B)-C(11)-H(11C)	111.3(17)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1

Table 34. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **21g**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^*2U^{11}+...+2hka^*b^*U^{12}]$

	U11	U22	U33	U23	U13	U12
O	12(1)	17(1)	18(1)	3(1)	5(1)	1(1)
C	14(1)	15(1)	17(1)	-1(1)	6(1)	0(1)
C	13(1)	16(1)	15(1)	0(1)	5(1)	0(1)
C	12(1)	14(1)	20(1)	2(1)	5(1)	1(1)
C	15(1)	21(1)	20(1)	4(1)	8(1)	1(1)
C	13(1)	18(1)	13(1)	-2(1)	4(1)	0(1)
C	17(1)	17(1)	18(1)	1(1)	6(1)	0(1)
C	17(1)	20(1)	18(1)	0(1)	4(1)	5(1)
C	14(1)	26(1)	13(1)	-4(1)	4(1)	1(1)
C	16(1)	23(1)	16(1)	0(1)	7(1)	-2(1)
C	16(1)	17(1)	16(1)	0(1)	5(1)	1(1)
C	16(1)	35(1)	22(1)	-2(1)	8(1)	3(1)

Table 35. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **21g**.

	X	Y	Z	U(eq)
H(1A)	4058(7)	-2630(20)	3662(10)	14(3)
H(1B)	4864(7)	-1610(20)	4016(9)	16(3)
H(3)	4444(7)	3840(20)	4531(10)	17(3)
H(4A)	3951(8)	3130(20)	2791(10)	22(3)
H(4B)	4656(8)	1440(20)	3067(10)	19(3)
H(6)	3122(8)	4140(20)	3278(10)	21(3)
H(7)	1951(8)	4570(30)	3220(10)	23(3)
H(9)	2028(8)	-1570(20)	4227(10)	21(3)
H(10)	3228(8)	-2040(20)	4327(10)	21(3)
H(11A)	956(11)	690(40)	3960(15)	61(6)
H(11B)	714(12)	1970(30)	2994(15)	58(6)
H(11C)	1086(12)	3150(40)	4037(16)	64(6)

Table 36. Torsional angles [°] for **21g**.

C(3)#1-O-C(1)-C(2)	-119.27(9)
O-C(1)-C(2)-C(5)	-69.90(11)
O-C(1)-C(2)-C(3)	76.48(11)
O-C(1)-C(2)-C(4)	141.74(9)
C(5)-C(2)-C(3)-O#1	145.81(10)
C(1)-C(2)-C(3)-O#1	-0.62(14)
C(4)-C(2)-C(3)-O#1	-105.32(11)
C(5)-C(2)-C(3)-C(4)	-108.87(11)
C(1)-C(2)-C(3)-C(4)	104.70(11)
O#1-C(3)-C(4)-C(2)	111.26(11)
C(5)-C(2)-C(4)-C(3)	105.89(11)
C(1)-C(2)-C(4)-C(3)	-106.29(10)
C(1)-C(2)-C(5)-C(10)	10.09(15)
C(3)-C(2)-C(5)-C(10)	-135.87(11)
C(4)-C(2)-C(5)-C(10)	157.18(10)
C(1)-C(2)-C(5)-C(6)	-171.26(10)
C(3)-C(2)-C(5)-C(6)	42.79(14)
C(4)-C(2)-C(5)-C(6)	-24.17(15)
C(10)-C(5)-C(6)-C(7)	0.39(16)
C(2)-C(5)-C(6)-C(7)	-178.31(10)
C(5)-C(6)-C(7)-C(8)	-0.61(17)
C(6)-C(7)-C(8)-C(9)	0.20(17)
C(6)-C(7)-C(8)-C(11)	179.94(10)
C(7)-C(8)-C(9)-C(10)	0.41(16)
C(11)-C(8)-C(9)-C(10)	-179.32(10)
C(8)-C(9)-C(10)-C(5)	-0.63(17)
C(6)-C(5)-C(10)-C(9)	0.22(16)
C(2)-C(5)-C(10)-C(9)	178.92(9)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1

A-2) Xray Data for [54ad]

Figure 11. ORTEP drawing of **54ad** showing 50% probability amplitude displacement ellipsoids.

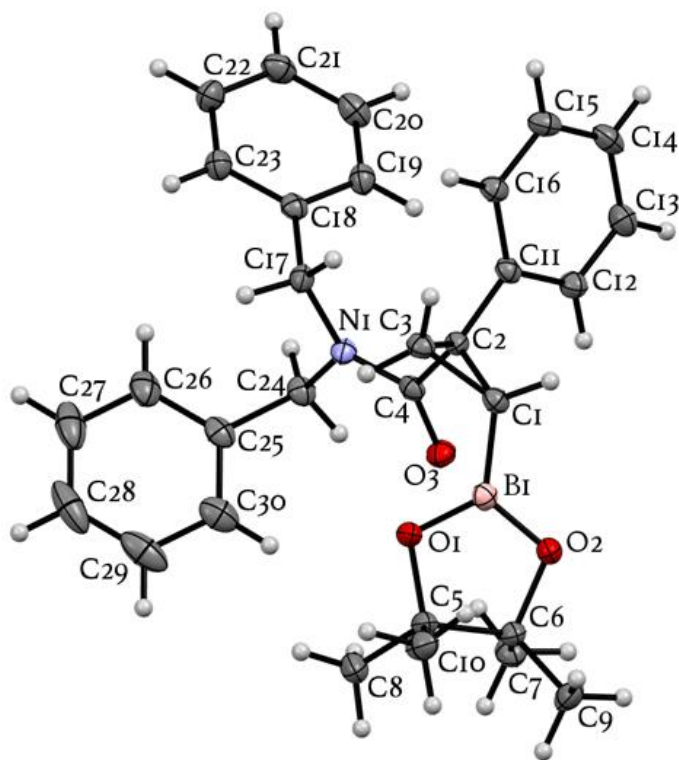


Figure 12. Packing of **54ad** molecules in the crystalline lattice.

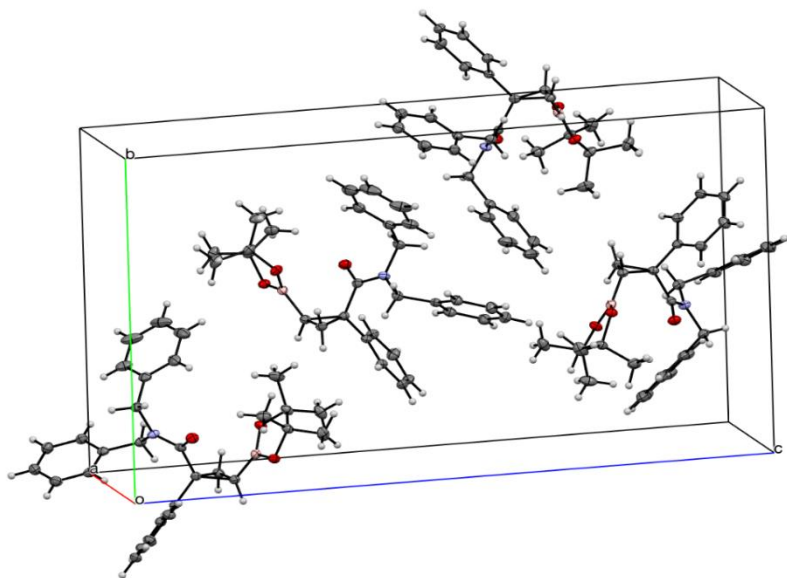


Table 37. Crystal data and structure refinement for **54ad**.

Empirical formula	C ₃₀ H ₃₄ BN ₃ O ₃
Formula weight	467.39
Temperature/K	100.02(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.45257(14)
b/Å	15.3580(3)
c/Å	25.9426(4)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2570.87(8)
Z	4
ρ _{calc} /cm ³	1.208
μ/mm ⁻¹	0.598
F(000)	1000.0
Crystal size/mm ³	0.325 × 0.111 × 0.066
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.688 to 148.374
Index ranges	-7 ≤ h ≤ 7, -17 ≤ k ≤ 19, -29 ≤ l ≤ 31
Reflections collected	23574
Independent reflections	5164 [R _{int} = 0.0515, R _{sigma} = 0.0389]
Data/restraints/parameters	5164/0/320
Goodness-of-fit on F ²	1.066
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0364, wR ₂ = 0.0871
Final R indexes [all data]	R ₁ = 0.0389, wR ₂ = 0.0892
Largest diff. peak/hole / e Å ⁻³	0.18/-0.17
Flack parameter	-0.04(10)

Table 38. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **54ad**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	X	Y	Z	U(eq)
O ²	5411(2)	5526.2(9)	2491.3(5)	20.1(3)
O ¹	2247(2)	6201.1(9)	2465.3(5)	21.3(3)
O ³	3344(3)	6102.9(9)	3617.0(6)	23.2(3)
N ¹	202(3)	5999.0(11)	4002.3(6)	18.7(4)
C ⁴	1722(3)	5698.9(12)	3690.6(7)	17.9(4)
C ²⁵	-827(4)	7562.0(13)	4034.4(8)	24.0(4)
C ¹⁵	691(4)	2771.3(14)	4273.0(8)	23.8(5)
C ²³	-4301(4)	5572.3(14)	4811.0(8)	23.0(4)
C ¹⁴	2621(4)	2707.4(14)	4502.0(8)	26.6(5)
C ¹²	3726(4)	3980.2(14)	4038.2(8)	22.5(4)
C ¹¹	1787(4)	4060.3(13)	3809.3(7)	18.6(4)
C ¹⁸	-2355(3)	5363.6(13)	4616.5(8)	19.5(4)
C ¹⁶	262(4)	3450.1(13)	3930.5(8)	20.6(4)
C ²⁴	476(4)	6841.5(13)	4265.9(8)	21.6(4)
C ¹⁹	-950(4)	4922.1(13)	4930.4(8)	23.5(4)
C ¹⁷	-1831(3)	5593.9(13)	4061.9(8)	19.9(4)
C ²⁰	-1515(4)	4681.2(14)	5427.5(9)	28.0(5)
C ¹	2344(3)	4706.3(13)	2902.5(7)	19.2(4)
C ¹³	4150(4)	3313.4(15)	4384.6(8)	27.3(5)
C ²¹	-3467(4)	4882.6(15)	5615.6(8)	28.8(5)
C ²	1434(3)	4804.4(12)	3442.2(7)	17.1(4)
C ²⁶	-2797(4)	7738.6(15)	4221.0(10)	32.0(5)
C ⁶	5818(3)	6401.9(13)	2294.1(8)	19.6(4)
C ²²	-4863(4)	5331.6(15)	5309.7(8)	27.9(5)
C ⁷	6798(4)	6920.1(14)	2731.0(9)	27.3(5)
C ⁹	7316(4)	6320.7(17)	1848.2(9)	28.7(5)
B ¹	3377(4)	5499.1(15)	2632.5(8)	18.9(5)
C ⁵	3607(4)	6728.0(14)	2142.4(8)	22.6(4)
C ⁸	3152(4)	7673.7(14)	2258.7(10)	32.1(5)
C ¹⁰	3029(4)	6526.7(16)	1582.6(8)	29.1(5)
C ³⁰	-59(5)	8052.1(15)	3623.1(9)	32.0(6)
C ²⁷	-4014(5)	8383.1(17)	3997.8(13)	45.1(7)
C ²⁸	-3252(6)	8863.0(16)	3588.6(12)	48.8(8)
C ²⁹	-1279(6)	8702.3(16)	3405.7(10)	43.6(8)
C ³	11(3)	4700.4(13)	2989.0(8)	20.2(4)

Table 39. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **54ad**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U11	U22	U33	U23	U13	U12
O ²	18.7(8)	17.4(7)	24.1(7)	1.6(5)	0.5(6)	1.5(6)
O ¹	17.6(8)	19.7(7)	26.6(7)	6.7(5)	2.4(6)	0.7(6)
O ³	19.2(8)	21.3(7)	29.0(7)	-1.4(6)	1.5(6)	-3.4(6)
N ¹	16.6(9)	15.9(8)	23.7(8)	-2.7(7)	0.2(6)	-1.6(7)
C ⁴	18.8(11)	16.5(9)	18.4(9)	2.3(7)	-3.7(7)	0.6(8)
C ²⁵	30.3(13)	16.0(9)	25.8(10)	-4.8(8)	-5.0(9)	-1.2(9)
C ¹⁵	32.4(14)	17.7(9)	21.3(9)	0.8(8)	3.2(8)	-4.6(9)
C ²³	23.0(12)	21.3(10)	24.8(10)	-1.2(8)	-0.1(8)	2.4(9)
C ¹⁴	40.3(15)	17.4(9)	22.2(10)	4.1(8)	0.3(9)	3.5(9)
C ¹²	21.2(12)	20.0(9)	26.3(10)	2.7(8)	-1.2(8)	-1.7(8)
C ¹¹	22.5(11)	13.8(8)	19.6(9)	-1.5(7)	0.8(8)	0.8(8)
C ¹⁸	21.8(11)	14.8(9)	21.8(9)	-2.2(7)	-0.9(7)	-1.6(8)
C ¹⁶	23.2(12)	17.0(9)	21.5(10)	-0.3(7)	-0.1(8)	-0.8(8)
C ²⁴	24.1(12)	17.5(9)	23.2(9)	-4.3(8)	-2.1(8)	-1.0(8)
C ¹⁹	21.6(12)	20.4(10)	28.6(10)	-2.6(8)	-1.6(8)	3.0(8)
C ¹⁷	16.3(11)	19.9(9)	23.5(9)	-2.0(8)	0.0(8)	1.4(8)
C ²⁰	36.7(14)	21.6(10)	25.6(10)	0.9(8)	-4.9(9)	3.6(10)
C ¹	22.3(11)	15.4(9)	19.8(9)	-0.7(7)	-0.3(7)	0.7(8)
C ¹³	27.0(13)	27.3(11)	27.7(10)	4.4(8)	-3.9(9)	4.4(10)
C ²¹	39.2(15)	24.4(11)	22.9(10)	2.1(8)	3.8(9)	0.3(10)
C ²	15.5(10)	15.0(9)	20.9(9)	0.5(7)	1.4(7)	0.2(8)
C ²⁶	30.8(15)	20.0(10)	45.3(13)	-7.5(9)	-2.3(10)	0.2(9)
C ⁶	16.5(11)	18.6(9)	23.8(9)	3.6(8)	1.0(8)	-0.8(8)
C ²²	27.2(13)	27.8(11)	28.9(11)	-1.1(9)	6.7(9)	3.0(10)
C ⁷	24.2(12)	22.8(10)	34.8(11)	0.0(9)	-4.5(9)	-2.5(9)
C ⁹	17.4(12)	40.3(13)	28.4(11)	6.2(9)	3.7(8)	1.3(10)
B ¹	20.5(12)	18.4(11)	17.8(10)	-1.3(8)	0.7(8)	1.5(9)
C ⁵	17.8(12)	22.8(10)	27.1(10)	8.3(8)	2.8(8)	0.3(8)
C ⁸	25.3(13)	22.4(11)	48.4(14)	7.3(10)	3.5(10)	4.0(10)
C ¹⁰	21.9(13)	38.0(12)	27.3(11)	10.5(9)	-3.4(9)	-2.7(10)
C ³⁰	47.9(17)	23.2(11)	24.8(10)	-3.8(9)	-5.7(10)	-3.5(10)
C ²⁷	35.3(17)	23.7(12)	76(2)	-15.3(13)	-15.6(14)	5.4(11)
C ²⁸	63(2)	21.4(12)	61.5(18)	-8.8(12)	-36.5(16)	10.5(13)
C ²⁹	76(2)	22.7(11)	32.4(13)	-0.1(10)	-20.1(13)	-3.6(13)
C ³	21.0(11)	17.1(9)	22.4(9)	0.8(8)	-1.8(7)	-2.6(8)

Table 40. Bond lengths [Å] for **54ad**.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
O ² -C ⁶	1.463(2)	C ¹¹ -C ²	1.505(3)
O ² -B ¹	1.363(3)	C ¹⁸ -C ¹⁹	1.395(3)
O ¹ -B ¹	1.372(3)	C ¹⁸ -C ¹⁷	1.520(3)
O ¹ -C ⁵	1.458(2)	C ¹⁹ -C ²⁰	1.390(3)
O ³ -C ⁴	1.231(3)	C ²⁰ -C ²¹	1.386(4)
N ¹ -C ⁴	1.352(3)	C ¹ -C ²	1.526(3)
N ¹ -C ²⁴	1.474(3)	C ¹ -B ¹	1.555(3)
N ¹ -C ¹⁷	1.460(3)	C ¹ -C ³	1.523(3)
C ⁴ -C ²	1.529(3)	C ²¹ -C ²²	1.385(3)
C ²⁵ -C ²⁴	1.514(3)	C ² -C ³	1.501(3)
C ²⁵ -C ²⁶	1.387(4)	C ²⁶ -C ²⁷	1.390(4)
C ²⁵ -C ³⁰	1.397(3)	C ⁶ -C ⁷	1.522(3)
C ¹⁵ -C ¹⁴	1.383(3)	C ⁶ -C ⁹	1.512(3)
C ¹⁵ -C ¹⁶	1.397(3)	C ⁶ -C ⁵	1.563(3)
C ²³ -C ¹⁸	1.391(3)	C ⁵ -C ⁸	1.512(3)
C ²³ -C ²²	1.394(3)	C ⁵ -C ¹⁰	1.531(3)
C ¹⁴ -C ¹³	1.390(3)	C ³⁰ -C ²⁹	1.391(4)
C ¹² -C ¹¹	1.390(3)	C ²⁷ -C ²⁸	1.383(5)
C ¹² -C ¹³	1.390(3)	C ²⁸ -C ²⁹	1.381(5)
C ¹¹ -C ¹⁶	1.395(3)		

Table 41. Bond angles for **54ad**.

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
B1-O2-C6	107.16(16)	C22-C21-C20	120.1(2)
B1-O1-C5	107.33(16)	C11-C2-C4	113.41(16)
C4-N1-C24	119.33(18)	C11-C2-C1	116.58(17)
C4-N1-C17	124.74(17)	C1-C2-C4	115.39(16)
C17-N1-C24	115.62(17)	C3-C2-C4	120.03(17)
O3-C4-N1	122.51(18)	C3-C2-C11	120.50(17)
O3-C4-C2	119.39(19)	C3-C2-C1	60.40(13)
N1-C4-C2	118.05(18)	C25-C26-C27	120.8(3)
C26-C25-C24	120.9(2)	O2-C6-C7	107.15(16)
C26-C25-C30	119.1(2)	O2-C6-C9	107.85(17)
C30-C25-C24	120.0(2)	O2-C6-C5	102.63(16)
C14-C15-C16	120.3(2)	C7-C6-C5	113.52(18)
C18-C23-C22	120.7(2)	C9-C6-C7	110.33(19)
C15-C14-C13	119.8(2)	C9-C6-C5	114.65(17)
C13-C12-C11	121.3(2)	C21-C22-C23	119.7(2)
C12-C11-C16	118.62(19)	O2-B1-O1	113.75(18)
C12-C11-C2	118.27(19)	O2-B1-C1	123.89(19)
C16-C11-C2	123.1(2)	O1-B1-C1	122.0(2)
C23-C18-C19	119.2(2)	O1-C5-C6	103.11(15)
C23-C18-C17	119.39(19)	O1-C5-C8	107.55(18)
C19-C18-C17	121.4(2)	O1-C5-C10	106.65(18)
C11-C16-C15	120.3(2)	C8-C5-C6	115.8(2)
N1-C24-C25	113.02(17)	C8-C5-C10	109.64(19)
C20-C19-C18	120.0(2)	C10-C5-C6	113.36(18)
N1-C17-C18	113.54(17)	C29-C30-C25	119.7(3)
C21-C20-C19	120.4(2)	C28-C27-C26	119.9(3)
C2-C1-B1	120.07(17)	C29-C28-C27	119.8(3)
C3-C1-C2	58.98(13)	C28-C29-C30	120.7(3)
C3-C1-B1	119.67(18)	C2-C3-C1	60.62(13)
C12-C13-C14	119.7(2)		

Table 42. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **54ad**.

Atom	x	y	z	U(eq)
H ¹⁵	-347	2352	4349	29
H ²³	-5258	5882	4602	28
H ¹⁴	2900	2251	4739	32
H ¹²	4780	4389	3956	27
H ¹⁶	-1075	3496	3780	25
H ^{24A}	1954	7011	4249	26
H ^{24B}	103	6773	4634	26
H ¹⁹	394	4786	4804	28
H ^{17A}	-1878	5057	3851	24
H ^{17B}	-2901	5996	3928	24
H ²⁰	-557	4377	5639	34
H ¹	2980	4127	2825	23
H ¹³	5479	3272	4540	33
H ²¹	-3847	4713	5955	35
H ²⁶	-3321	7415	4505	38
H ²²	-6198	5475	5439	34
H ^{7A}	5858	6927	3028	41
H ^{7B}	7054	7518	2616	41
H ^{7C}	8113	6649	2831	41
H ^{9A}	8650	6103	1975	43
H ^{9B}	7513	6893	1688	43
H ^{9C}	6754	5914	1593	43
H ^{8A}	1683	7793	2195	48
H ^{8B}	4003	8045	2036	48
H ^{8C}	3476	7796	2621	48
H ^{10A}	3228	5904	1516	44
H ^{10B}	3915	6866	1351	44
H ^{10C}	1575	6681	1523	44
H ³⁰	1291	7942	3492	38
H ²⁷	-5368	8494	4126	54
H ²⁸	-4083	9302	3434	59
H ²⁹	-749	9039	3128	52
H ^{3A}	-786	5217	2876	24
H ^{3B}	-725	4138	2951	24

A-3) Xray Data for [83aa]

Figure 13. ORTEP drawing of **83aa** showing 50% probability amplitude displacement ellipsoids.

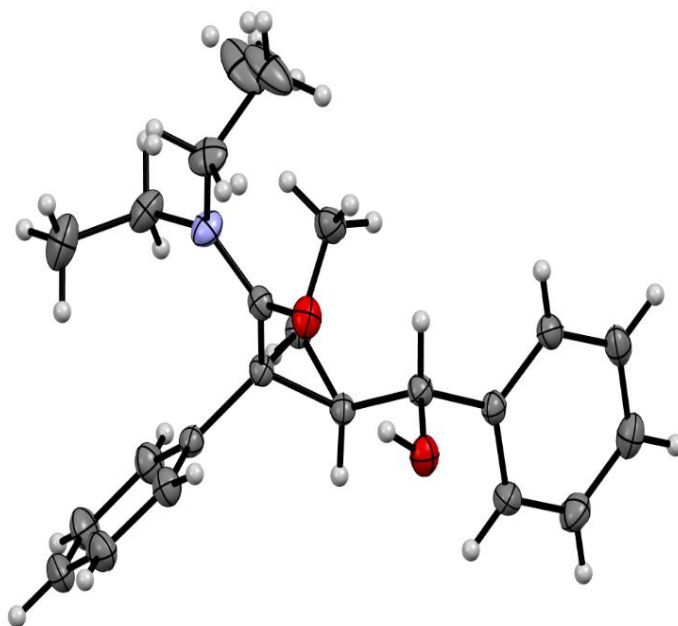


Figure 14. Packing of **83aa** molecules in the crystalline lattice.

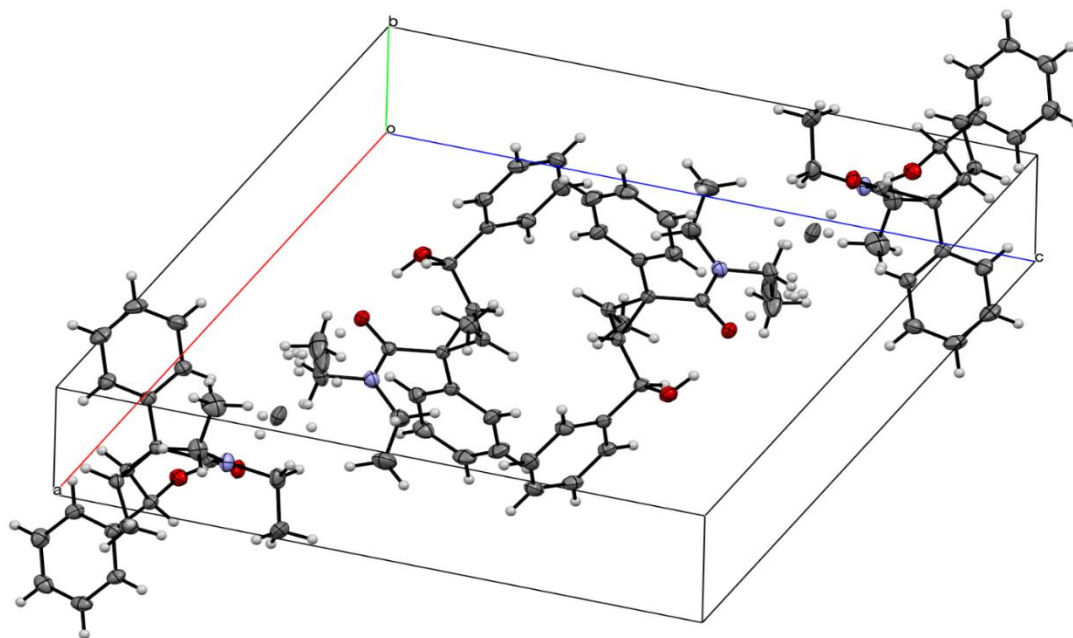


Table 43. Crystal data and structure refinement for **83aa**.

Empirical formula	C ₂₂ H ₂₇ NO ₂
Formula weight	337.44
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	14.9999(2)
b/Å	7.56312(8)
c/Å	17.9960(3)
α/°	90
β/°	113.2748(18)
γ/°	90
Volume/Å ³	1875.43(5)
Z	4
ρ _{calc} /g/cm ³	1.195
μ/mm ⁻¹	0.592
F(000)	728.0
Crystal size/mm ³	0.451 × 0.301 × 0.252
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.848 to 152.316
Index ranges	-18 ≤ h ≤ 18, -9 ≤ k ≤ 7, -22 ≤ l ≤ 22
Reflections collected	13759
Independent reflections	3897 [R _{int} = 0.0184, R _{sigma} = 0.0147]
Data/restraints/parameters	3897/0/244
Goodness-of-fit on F ²	1.021
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0366, wR ₂ = 0.0902
Final R indexes [all data]	R ₁ = 0.0399, wR ₂ = 0.0942
Largest diff. peak/hole / e Å ⁻³	0.27/-0.19

Table 44. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **83aa**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
O001	3924.3(5)	3541.7(10)	7284.8(4)	26.52(17)
O002	5048.6(5)	945.7(10)	6936.0(4)	26.57(17)
N003	3176.9(7)	6101.5(12)	6742.8(5)	26.0(2)
C004	3649.0(7)	4105.9(13)	5892.9(5)	18.4(2)
C005	6289.3(7)	2164.5(13)	6564.7(6)	20.8(2)
C006	4551.9(7)	3165.0(13)	5897.1(6)	19.2(2)
C007	5356.0(7)	2538.6(13)	6671.6(6)	20.4(2)
C008	3600.7(7)	4562.5(13)	6697.2(6)	20.1(2)
C009	2683.8(7)	3524.3(13)	5266.6(6)	20.0(2)
C00A	4385.7(7)	5083.5(13)	5655.0(6)	20.8(2)
C00B	6321.8(8)	967.3(14)	5987.4(6)	26.2(2)
C00C	7140.6(7)	3022.4(14)	7055.5(6)	24.2(2)
C00D	2095.3(8)	2418.6(15)	5499.1(6)	26.1(2)
C00E	2351.2(8)	4052.1(15)	4463.0(6)	28.0(2)
C00F	5016.4(8)	6525.0(15)	6184.2(7)	28.1(2)
C00G	8008.1(7)	2699.7(15)	6967.9(7)	28.0(2)
C00H	8026.8(8)	1522.3(16)	6388.2(7)	30.6(2)
C00I	7185.5(8)	652.1(16)	5897.3(7)	31.0(2)
C00J	1191.5(8)	1884.5(16)	4941.1(7)	32.3(2)
C00K	870.6(8)	2411.7(17)	4140.9(7)	34.0(3)
C00L	3182.0(9)	6659.1(16)	7527.3(7)	33.1(3)
C00M	1453.5(9)	3488.5(17)	3904.3(7)	34.3(3)
C00N	2709.3(9)	7309.9(15)	6061.7(7)	31.8(3)
C00O	1608.5(10)	7218(2)	5738.5(9)	46.0(3)
C00P	4124(7)	7692(14)	8044(6)	52.3(15)
C00Q	3880(13)	8010(30)	7864(10)	53(3)

Table 45. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **83aa**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U11	U22	U33	U23	U13	U12
O001	28.4(4)	33.9(4)	18.7(3)	4.8(3)	10.8(3)	5.3(3)
O002	25.8(4)	27.6(4)	25.5(4)	6.0(3)	9.3(3)	1.9(3)
N003	31.2(5)	26.6(4)	24.5(4)	-0.6(3)	15.6(4)	4.0(4)
C004	19.2(4)	20.0(4)	15.9(4)	0.8(3)	6.8(4)	1.6(3)
C005	20.2(5)	21.2(5)	18.6(4)	1.9(4)	5.2(4)	3.3(4)
C006	18.5(4)	22.4(5)	16.6(4)	-1.1(3)	6.7(4)	1.5(4)
C007	20.5(5)	21.9(5)	17.0(4)	-0.1(3)	5.4(4)	1.5(4)
C008	18.0(4)	24.7(5)	18.2(4)	-0.6(4)	7.7(3)	-1.4(4)
C009	19.4(4)	20.6(5)	18.7(4)	0.0(4)	6.1(4)	3.3(4)
C00A	20.7(4)	24.0(5)	18.9(4)	2.0(4)	9.0(4)	1.0(4)
C00B	23.4(5)	26.3(5)	25.5(5)	-4.3(4)	6.1(4)	1.5(4)
C00C	23.7(5)	24.1(5)	20.8(5)	0.3(4)	4.3(4)	1.7(4)
C00D	24.4(5)	29.6(5)	24.8(5)	0.8(4)	10.3(4)	-0.6(4)
C00E	27.5(5)	31.6(6)	21.0(5)	4.4(4)	5.4(4)	1.0(4)
C00F	26.7(5)	26.0(5)	32.8(6)	-1.7(4)	13.0(4)	-4.6(4)
C00G	19.9(5)	28.4(5)	30.5(5)	5.9(4)	4.3(4)	0.2(4)
C00H	24.5(5)	32.4(6)	37.2(6)	7.7(5)	14.7(5)	7.0(4)
C00I	32.4(6)	30.8(6)	31.8(6)	-2.5(4)	14.9(5)	7.2(4)
C00J	23.9(5)	35.2(6)	37.7(6)	-4.4(5)	12.1(5)	-5.0(4)
C00K	20.7(5)	38.1(6)	34.3(6)	-8.5(5)	1.4(4)	0.8(4)
C00L	41.7(6)	34.4(6)	32.9(6)	-6.5(5)	25.2(5)	0.4(5)
C00M	30.9(6)	40.4(7)	22.3(5)	1.0(5)	0.5(4)	2.9(5)
C00N	38.9(6)	25.4(5)	36.3(6)	5.2(4)	20.4(5)	9.5(5)
C00O	38.8(7)	47.0(8)	54.6(8)	11.7(6)	20.9(6)	18.6(6)
C00P	48(3)	83(3)	28(3)	-21(2)	17(2)	-29(2)
C00Q	44(6)	97(7)	23(5)	-20(4)	17(4)	-16(4)

Table 46. Bond lengths [Å] for **83aa**.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
O001-C008	1.2427(12)	C009-C00D	1.3947(14)
O002-C007	1.4366(12)	C009-C00E	1.3891(14)
N003-C008	1.3442(14)	C00A-C00F	1.5095(14)
N003-C00L	1.4707(13)	C00B-C00I	1.3883(15)
N003-C00N	1.4663(14)	C00C-C00G	1.3928(15)
C004-C006	1.5273(13)	C00D-C00J	1.3905(15)
C004-C008	1.5175(12)	C00E-C00M	1.3913(16)
C004-C009	1.5067(13)	C00G-C00H	1.3803(17)
C004-C00A	1.5248(13)	C00H-C00I	1.3875(17)
C005-C007	1.5132(13)	C00J-C00K	1.3843(18)
C005-C00B	1.3934(14)	C00K-C00M	1.3796(18)
C005-C00C	1.3930(14)	C00L-C00P	1.560(9)
C006-C007	1.5144(13)	C00L-C00Q	1.417(18)
C006-C00A	1.5071(14)	C00N-C00O	1.5201(18)

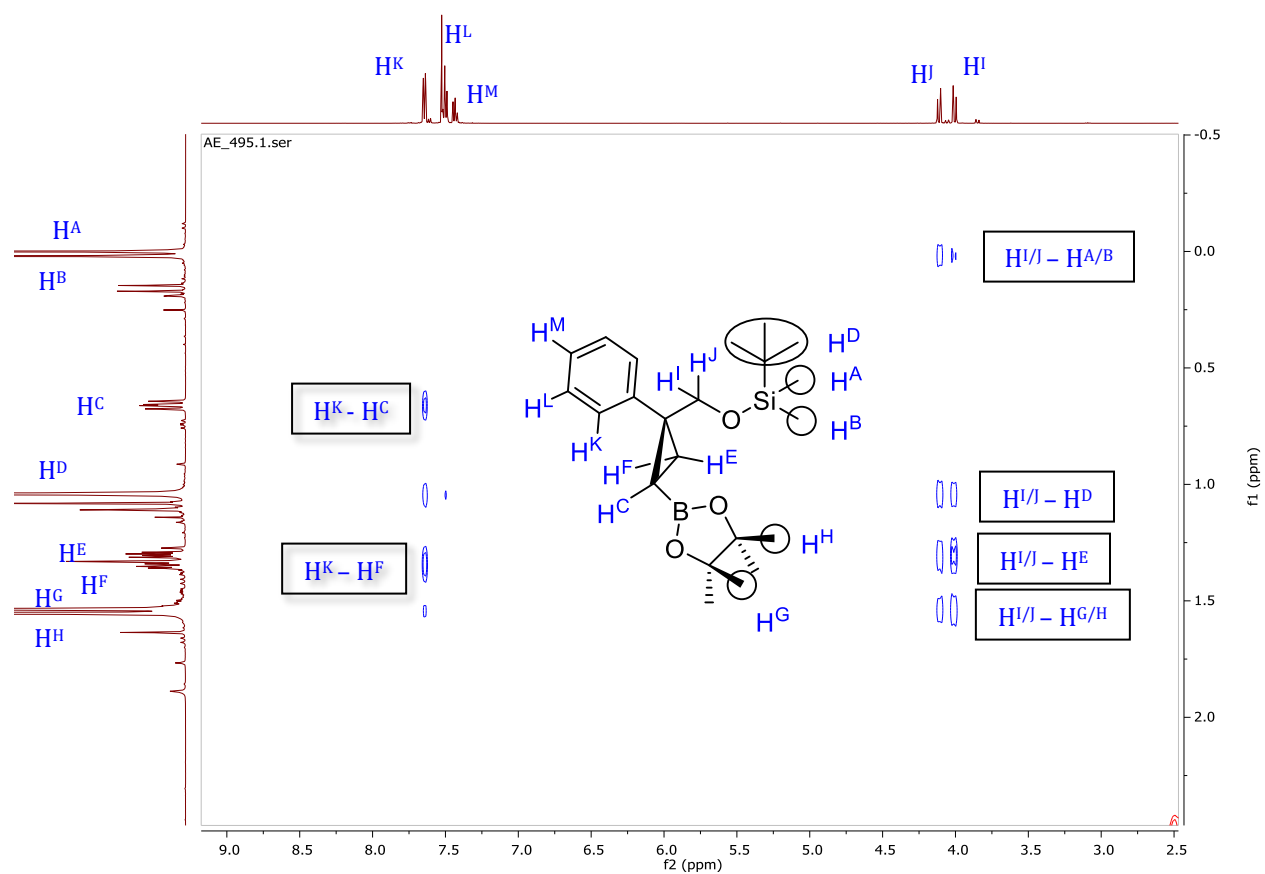
Table 47. Bond angles for **83aa**.

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
C008-N003-C00L	118.92(9)	N003-C008-C004	117.21(8)
C008-N003-C00N	124.77(9)	C00D-C009-C004	119.06(9)
C00N-N003-C00L	116.30(9)	C00E-C009-C004	122.58(9)
C008-C004-C006	118.54(8)	C00E-C009-C00D	118.36(9)
C008-C004-C00A	118.07(8)	C006-C00A-C004	60.49(6)
C009-C004-C006	117.11(8)	C006-C00A-C00F	121.48(9)
C009-C004-C008	112.71(8)	C00F-C00A-C004	121.07(8)
C009-C004-C00A	121.36(8)	C00I-C00B-C005	120.52(10)
C00A-C004-C006	59.18(6)	C00G-C00C-C005	120.66(10)
C00B-C005-C007	121.54(9)	C00J-C00D-C009	120.64(10)
C00C-C005-C007	119.64(9)	C009-C00E-C00M	120.75(11)
C00C-C005-C00B	118.82(9)	C00H-C00G-C00C	119.84(10)
C007-C006-C004	122.17(8)	C00G-C00H-C00I	120.14(10)
C00A-C006-C004	60.33(6)	C00H-C00I-C00B	120.01(10)
C00A-C006-C007	123.22(8)	C00K-C00J-C00D	120.43(11)
O002-C007-C005	108.63(8)	C00M-C00K-C00J	119.26(10)
O002-C007-C006	108.91(8)	N003-C00L-C00P	112.1(3)
C005-C007-C006	112.45(8)	C00Q-C00L-N003	109.9(6)
O001-C008-N003	121.42(9)	C00K-C00M-C00E	120.55(11)
O001-C008-C004	121.36(9)	N003-C00N-C00O	112.32(10)

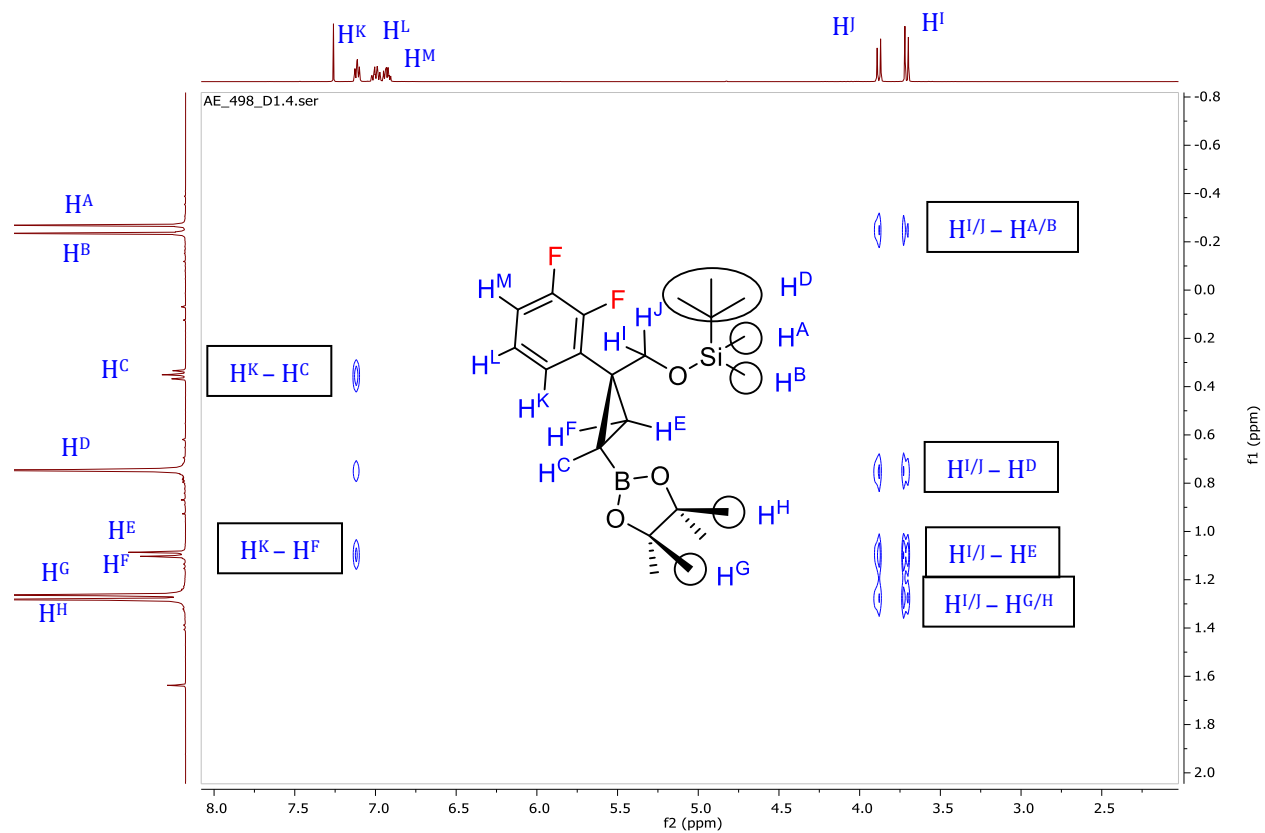
Table 48. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **83aa**.

Atom	x	y	z	U(eq)
H006	4419.76	2357.96	5439.72	23
H007	5478.95	3449.46	7087.84	24
H00A	4173.16	5296.18	5073.06	25
H00B	5760.57	374.65	5659.92	31
H00C	7129.56	3818.55	7445.66	29
H00D	2309.46	2034.92	6032.38	31
H00E	2732.82	4790.46	4296.51	34
H00F	4687.83	7639.95	6034.76	42
H00G	5618.02	6575.67	6114.14	42
H00H	5144.46	6276.03	6740.17	42
H00I	8573.32	3276.11	7299.12	34
H00J	8604.65	1311.76	6326.54	37
H00K	7200.08	-142.45	5507.86	37
H00L	800.1	1168.44	5106.57	39
H00M	268.78	2044.07	3767.08	41
H00N	3127.79	5623.64	7824.83	40
H00O	2622.43	7405.04	7436.25	40
H00P	2544.25	7092.74	7454.68	40
H00Q	3334.78	5656.37	7892.71	40
H00R	1244.65	3840.68	3366.94	41
H00S	2917.53	7017.24	5630.29	38
H00T	2916.7	8509.83	6234.86	38
H00U	1333.77	8026.85	5294.96	69
H00V	1397.81	7529.94	6160.35	69
H00W	1398.64	6037.61	5556.05	69
H00X	4672.54	6914.37	8191.11	78
H00Y	4070.1	8133.24	8525.3	78
H	4207.97	8663.89	7735.26	78
H00Z	4501.75	7607.87	7896.78	80
HA	3920.98	8294.26	8396.8	80
HB	3691.88	9043.38	7528.27	80
H002	4590(12)	1330(20)	7089(10)	47(4)

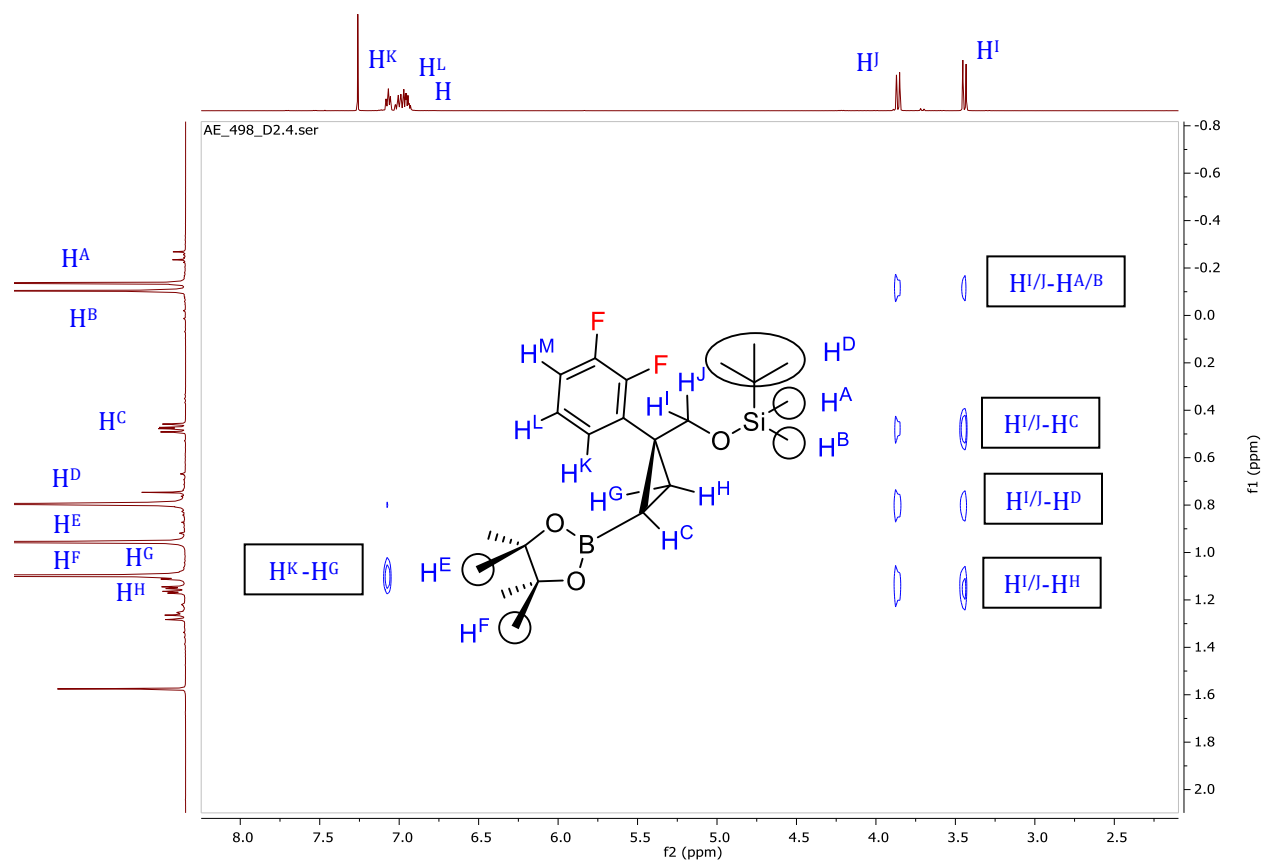
A-4) ^1H - ^1H 2D NOESY NMR of [46]



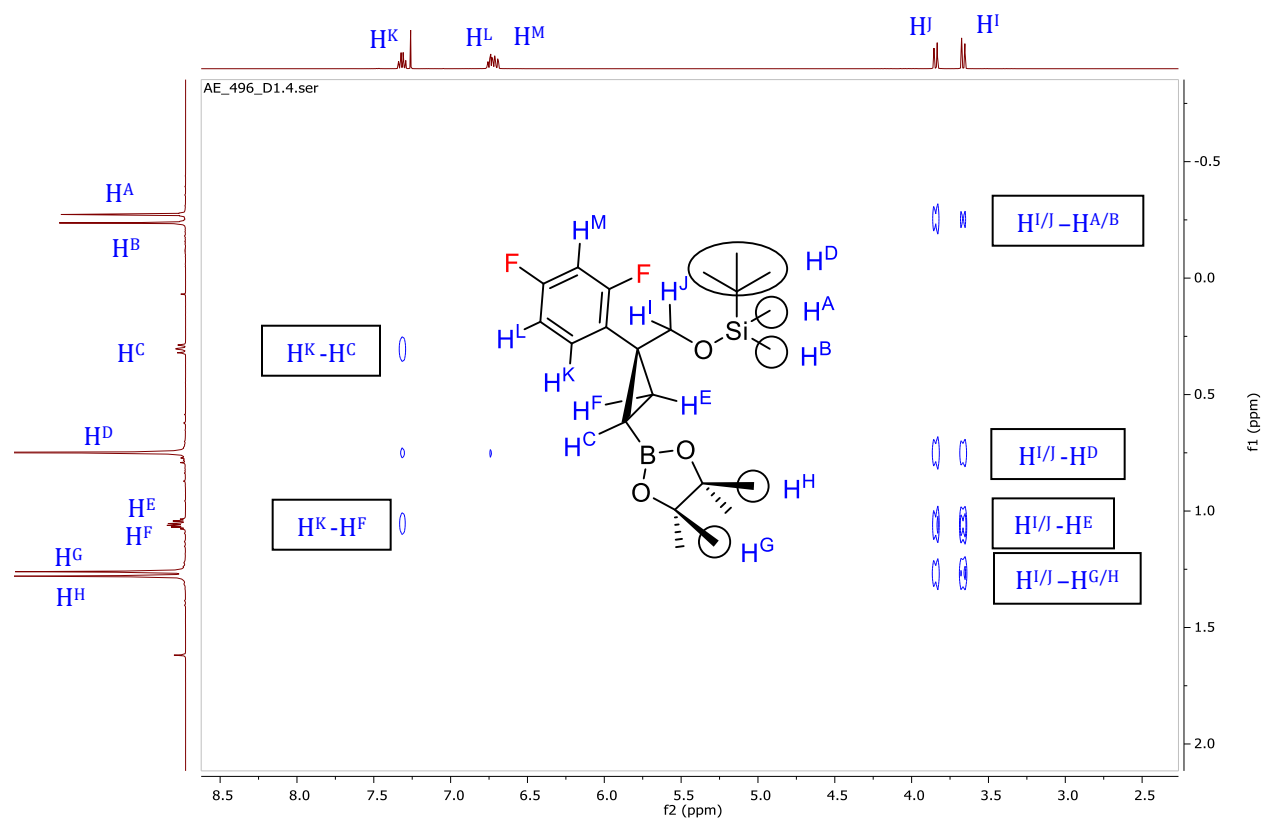
A-5) ^1H - ^1H 2D NOESY NMR of [63] major



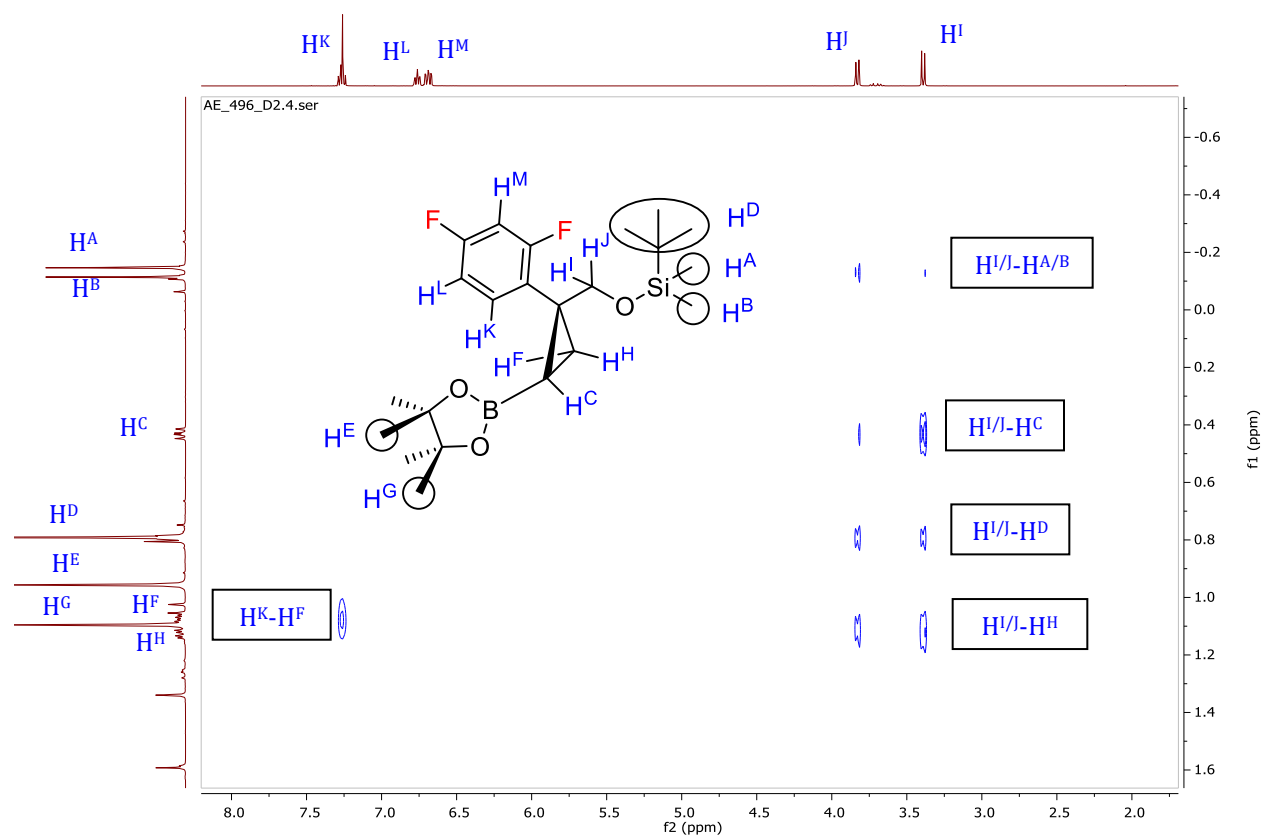
A-6) ^1H - ^1H 2D NOESY NMR of [63] minor



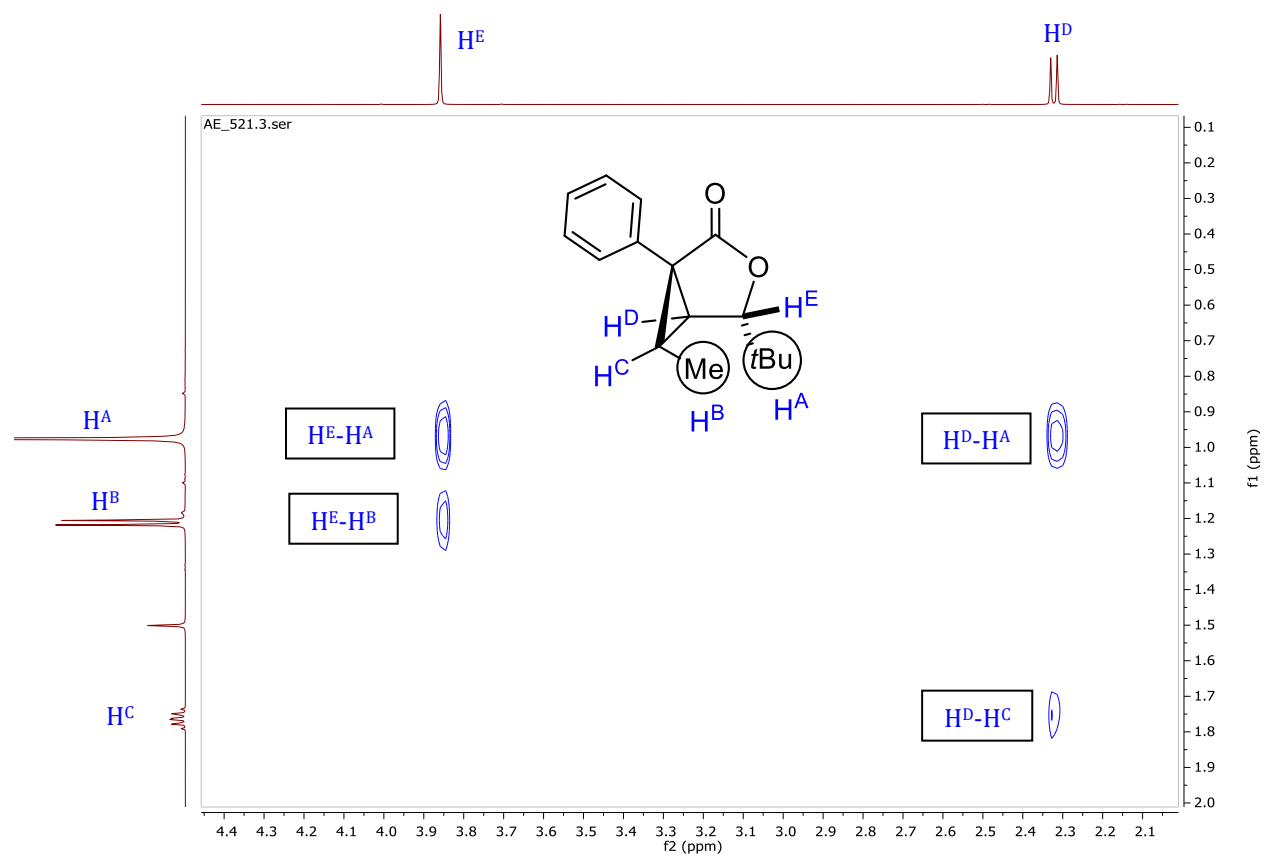
A-7) ^1H - ^1H 2D NOESY NMR of [64] major



A-8) ^1H - ^1H 2D NOESY NMR of [64] minor



A-9) ^1H - ^1H 2D NOESY NMR of [85]



A-10) Chiral HPLC Data

Chiral HPLC analysis was conducted with either a Rainin Dynamax SD-200 equipped with a 250mm x 4.6mm Chiracel OD-H column and Rainin Dynamax Absorbance detector UV-C set at 254nm or Agilent Technologies 1220 Infinity system equipped with either Diacel Chirapak IC, Diacel Chirapak IE, or Diacel Chirapak IB. Columns are Identified as follows:

Column 1: Chiracel OD-H (Eluent flow rate 0.5 mL/min)

Column 2: Diacel Chirapak IC (Eluent flow rate 1.0 mL/min)

Column 3: Diacel Chirapak IE (Eluent flow rate 1.0 mL/min)

Column 4: Diacel Chirapak IB (Eluent flow rate 1.0 mL/min)

All analytical methods were optimized using racemic hydroboration products obtained via the same procedure as described in the experimental for asymmetric hydroboration except with racemic BINAP ligand used instead of asymmetric ligand. Crude reaction mixtures were filtered through a short column of silica gel and analyzed without further purification.

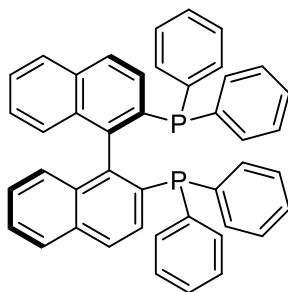
Compound	Column	Eluent (Hexane/IPA)	R _t of Enantiomers (min)
32a	1	(99.5/0.5)	10.65; 12.89
32b	1	(99.5/0.5)	12.11; 16.88
32c	2	(95/5)	4.27; 4.61 ^[a] 5.95; 6.33 ^[b]
32d	1	(99.5/0.5)	11.39; 14.61
32e	1	(99.5/0.5)	12.03; 16.11
32f	1	(99.9/0.1)	36.30; 43.17
32g	1	(99.5/0.5)	11.12; 15.68
32i	1	(99.5/0.5)	12.38; 18.97
32j	2	(95/5)	4.12; 4.34 ^[a] 5.02; 5.35 ^[b]
32k	1	(99.5/0.5)	11.76; 14.89
32l	1	(99.5/0.5)	11.74; 15.68
32m	1	(99.5/0.5)	11.12; 14.42
32n	1	(99.5/0.5)	9.84; 13.04
32o	2	(95/5)	3.92; 4.23

44	2	(97:3)	4.38; 4.85
45	2	(97:3)	5.26; 5.79
46	4	(99.6/0.4)	3.48; 4.13
54aa	2	(80/20)	5.75; 8.62
54ab	2	(80/20)	5.58; 6.09
54ad	2	(80/20)	5.36; 7.58
54ae	2	(80/20)	6.03; 7.81
54af	2	(80/20)	5.68; 6.43
54ai	2	(80/20)	6.86; 8.98
54ak	2	(80/20)	8.33; 9.74
54am	2	(80/20)	4.60; 5.27
54an	2	(90/10)	6.27; 7.94
54ao	2	(97.5/2.5)	8.08; 10.20 ^[a] 8.74; 11.27 ^[b]
54ar	2	(90/10)	6.69; 7.65
54au	2	(95/5)	15.32; 16.84
54fa	2	(80/20)	6.17; 8.55
54ga	2	(80/20)	6.64; 11.13
54ba	2	(80/20)	5.04; 8.32
54la	2	(80/20)	5.06; 9.01
54na	2	(80/20)	4.28; 10.62
54ia	2	(80/20)	5.75; 8.62
54ja	2	(80/20)	5.65; 11.88
54ca	2	(80/20)	5.31; 7.80
54da	2	(80/20)	5.89; 10.66
54oa	3	(90/10)	11.22; 8.72
54ma	2	(80/20)	5.70; 14.02
54ea	2	(80/20)	5.79; 13.35
57	2	(80/20)	7.96; 16.29
63 (<i>cis</i>)	4	(99.6/0.4)	3.50; 3.62
63 (<i>trans</i>)	4	(99.6/0.4)	3.54; 3.70
64 (<i>cis</i>)	4	(99.8/0.2)	4.40; 6.19
64 (<i>trans</i>)	4	(99.6/0.4)	3.13; 3.61
66	2	(97:3)	3.77; 3.98
67	4	(99/1)	4.13; 4.38

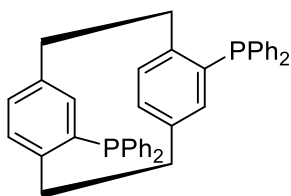
[a] Major diastereomer. [b] Minor diastereomer.

A-11 Structures of Chiral Ligands

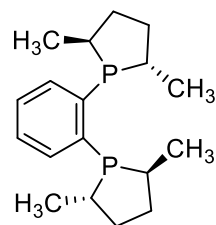
(R)-BINAP



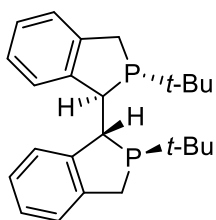
(S)-Phanephos



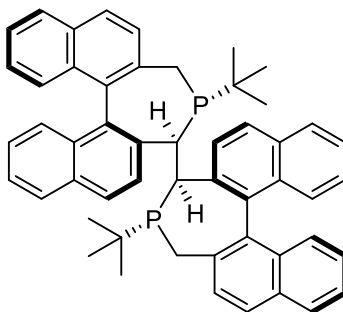
(S,S)-Me-DUPHOS



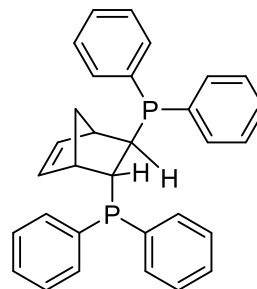
(R,R,S,S)-DuanPhos



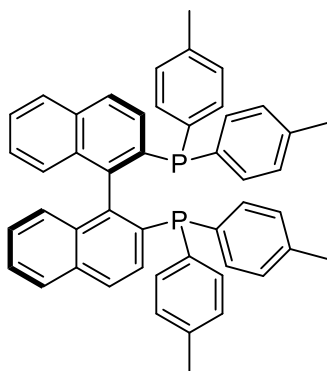
(S)-Binapine



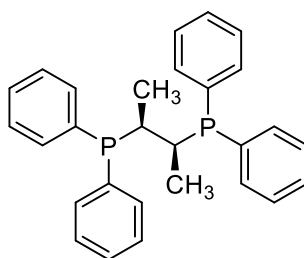
(R,R)-NORPHOS



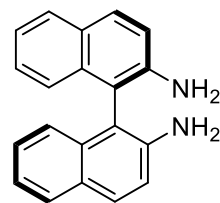
(R)-Tol-BINAP



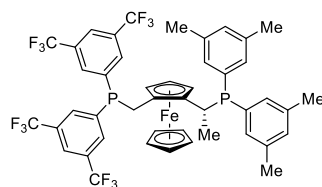
(S,S)-Chiraphos



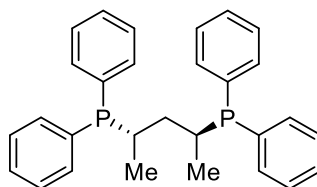
(R)-BINAM



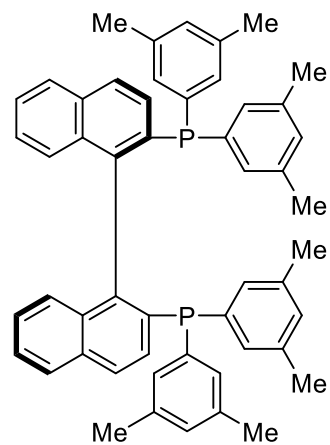
Josiphos
(SL-J008-1)



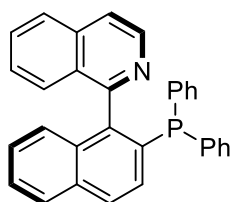
(*S,S*)-BDPP



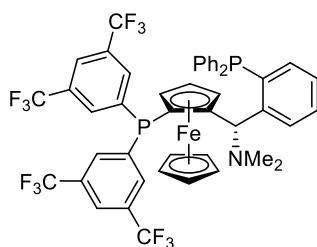
(*R*)-DM-BINAP



(*R*)-Quinap



TaniaPhos
SL-T001-1



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- [5] Edwards, A.; Rubina, M.; Rubin, M. Directed Rh(I)-Catalyzed Asymmetric Hydroboration of Prochiral 1-Arylcycloprop-2-ene-1-carboxylic Acid Derivatives. *Chem. Eur. J.* **2018**, *24*, 1394–1403.
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